MANY BODY PERTURBATION THEORY USING A RESTRICTED OPEN-SHELL HARTREE-FOCK (ROHF) REFERENCE FUNCTION

By

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One of the most common reference functions used for open shell molecules is the unrestricted Hartree-Fock (UHF) reference. While this reference is useful for many molecular systems, it can sometimes suffer from the mixing of higher multiplicity states into the state of interest. This phenomenon is termed spin contamination. A number of projection techniques have been developed to correct the UHF reference at the SCF and correlated levels. General implementation of gradients for these projected methods, however, can be complex and computationally expensive. Nor are such methods rigorously extensive, as required for many-electron methods. These facts limit the usefulness of these methods.

This work presents the development of an alternative approach. Rather than attempting to correct the deficiencies in the UHF reference, we start with a reference (ROHF) which is an eigenfunction of spin. The treatment of electron correlation is introduced using many body perturbation theory (MBPT), which is perhaps the most efficient way of adding the critical effects of electron correlation. This development is taken from the coupled cluster (CC) perspective. While others have used this

reference to conduct MBPT calculations, we present a more general derivation which avoids one of the drawbacks of previous work, namely the requirement of an iterative solution for the wavefunction and energy. By exploiting the invariance of the CC (MBPT) energy to rotations in the occupied-occupied and virtual-virtual spaces, one can obtain equations which lead to the solution for the wavefunction in a *non-iterative* fashion. Additionally, this derivation leads to an efficient formulation for ROHF-MBPT gradients, also taken from the CC perspective.

This dissertation presents a new development in treating electron correlation. First, there is the derivation of a general ROHF based MBPT for energies and gradients. Second, these methods have been implemented through full fourth order in MBPT for energies, and through third order for gradients in the ACES II program system. Third, these methods have been applied to selected molecular problems where a spin contaminated UHF reference is known to give poor results for MBPT. For these cases, ROHF based MBPT has shown considerable improvement when compared to experiment or more complete correlation treatments. These methods therefore offer an opportunity to conduct correlated studies on molecular systems and obtain reasonable results when UHF based schemes would not.

CHAPTER 1
INTRODUCTION

Many body perturbation theory (MBPT) [1, 2] is well known to offer a highly efficient correlation approximation for many problems in the electronic structure of molecules. For it to be sufficiently accurate in low orders, however, the reference function has to offer a reasonably good approximation for the problem of interest. For open-shell systems, unrestricted Hartree-Fock (UHF) has usually served as the reference [1, 2, 3, 4, 5]. Such methods which relax the restriction of having identical α and β orbitals and can relax other symmetry restrictions have certain advantages, notably in bond breaking situations. However, they also have several disadvantages. Besides the frequent existence of several different UHF solutions, UHF functions are not eigenfunctions of spin, as they are contaminated by states of higher spin multiplicity. The infinite-order coupled-cluster generalizations of MBPT like CCSD [6], and particularly CCSDT [7, 8] and its approximations, CCSDT-n [9], CCSD+T(CCSD) [10], and CCSD(T) and others [11, 12] have a great capacity to eliminate spin contamination [13, 14, 15], but the efficient and inexpensive non-iterative MBPT(n) approximations do not [1, 2].

Because of this problem, various UHF based MBPT spin-projected methods have been developed [15, 16, 17, 18, 19, 20], where one or more contaminating multiplicities are removed from the UHF/MBPT(2) solution. This procedure, however, is difficult to apply in higher orders of MBPT. Furthermore, the spin-projected MBPT methods will not usually be size-extensive. Also, since projection does not correctly preserve

order, ambiguities can occur in determining relative energy differences between open- and closed-shell molecules at a given MBPT(n) level. Finally, building analytical gradients upon such projected approaches [19, 20], an integral part of any widely used method in quantum chemistry, is difficult for even MBPT(2) [20].

A much more general approach to eliminate spin contamination in open-shell systems is to start from a spin-eigenfunction, such as a high-spin restricted open-shell Hartree-Fock (ROHF) reference. Such an ROHF based MBPT was proposed by Hubac and Carsky [21], but has the disadvantage of redefining H_0 as a sum of diagonal generalized Fock operators, which changes the meaning of MBPT(n) from that in the usual canonical (Moller-Plesset) Hartree-Fock case and loses certain invariant properties. An alternative route is to correct the reference via a generalized MBPT that retains some of the essential elements of CC theory. This approach derives from that used by Laidig, Purvis, and Bartlett [22] for localized orbitals, and a related approach of Wolinski and Pulay [23]. It is also a special case of the ROHF-CC method originally proposed by Bartlett and co-workers [24, 25]. The approach of Laidig, et al. [22] was primarily concerned with CC solutions, which unlike MBPT(n), are independent of any choice of H_0. Hence, using a sum of diagonal Fock operators as H_0 was satisfactory for CC theory, but changes the meaning of finite order MBPT(n) results and their invariance properties. The method of Wolinski and Pulay [23] retains the correspondence to each order in MBPT with the canonical Hartree-Fock reference case, but at the cost of an off-diagonal resolvent operator which requires an iterative solution for the amplitudes. The cost for an iterative solution is modest, except that to provide a high accuracy method, it is necessary to include the triples contribution in MBPT(4). An iterative inclusion of this expensive N^7 step would be impractical, recommending a non-iterative approach. Furthermore, our approach is readily generalizable to any order of perturbation theory. Rather than a spin-adapted approach

as used by Wolinski and Pulay [23], our approach is based upon a spin orbital formulation like the ROHF-CC [24] method which enables treating any order. This gives it the projected spin eigenfunction property $\langle ROHF|\hat{S}^2|\Psi_{MBPT}\rangle = S(S+1)$. The expectation value of Ψ_{MBPT} is not $S(S+1)$, though. Additionally, our approach retains the invariance properties of MBPT/CC theory to transformations among just occupied or unoccupied orbitals. Consequently, facilitated by the latter point, analytical gradients can easily be developed for the proposed ROHF-MBPT methods [26], built upon the recently proposed ROHF-CC formalism [27].

The remainder of this work will cover the theoretical development of ROHF based MBPT energies and gradients through full fourth order. This will be followed by representative examples of molecular systems where it is appropriate to consider using these ROHF based methods. In particular, the use of ROHF-MBPT(2) and ROHF-CCSD gradients for geometry optimization followed by single-point energy calculations through ROHF-MBPT(4) are presented. These results will demonstrate the usefulness of this new approach to electron correlation.

CHAPTER 2

ROHF-MBPT ENERGIES

In this chapter, only the expressions for the correlation energy will be derived. A discussion of the ROHF reference itself can be found in reference [28]. As the starting point for the derivation of the formulas for ROHF-MBPT, we use the full CCSD equations. In particular, the most efficient approach to implementing these equations with symmetry has been shown to be the direct product decomposition (DPD) method [29]. In the following, we follow the conventions that i, j, k, ... represent occupied orbitals; a, b, c, ... represent unoccupied orbitals; and p, q, r, ... are generic indices representing either kind of orbital. The explicit equations for the CCSD model in fully factored spin-orbital form are presented below.

T_1 equation:

$$\begin{aligned} t_i^a D_i^a &= f_{ia} + \sum_e t_i^e \mathcal{F}_{ae} - \sum_m t_m^a \mathcal{F}_{mi} + \sum_{me} t_{im}^{ae} \mathcal{F}_{me} - \sum_{nf} t_n^f \langle na \| if \rangle \\ &\quad - \frac{1}{2} \sum_{mef} t_{im}^{ef} \langle ma \| ef \rangle - \frac{1}{2} \sum_{men} t_{me}^{ae} \langle nm \| ei \rangle \end{aligned} \tag{2.1}$$

T_2 equation:

$$\begin{aligned} t_{ij}^{ab} D_{ij}^{ab} &= \langle ij \| ab \rangle + P(ab) \sum_e t_{ij}^{ae} \left(\mathcal{F}_{be} - \frac{1}{2} \sum_m t_m^b \mathcal{F}_{me} \right) \\ &\quad - P(ij) \sum_m t_{im}^{ab} \left(\mathcal{F}_{mj} + \frac{1}{2} \sum_e t_j^e \mathcal{F}_{me} \right) + \frac{1}{2} \sum_{mn} \tau_{mn}^{ab} \mathcal{W}_{mnij} \end{aligned}$$

$$+\frac{1}{2}\sum_{ef}\tau_{ij}^{ef}\mathcal{W}_{abef}+P(ij)P(ab)\sum_{me}(t_{im}^{ae}\mathcal{W}_{mbej}-t_i^e t_m^a\langle mb\|ej\rangle)$$
$$+P(ij)\sum_{e}t_i^e\langle ab\|ej\rangle-P(ab)\sum_{m}t_m^a\langle mb\|ij\rangle \tag{2.2}$$

Definition of $\mathcal{F}$ and $\mathcal{W}$ intermediates:

$$\mathcal{F}_{ae}=(1-\delta_{ae})f_{ae}-\frac{1}{2}\sum_{m}f_{me}t_m^a+\sum_{mf}t_m^f\langle ma\|fe\rangle-\frac{1}{2}\sum_{mnf}\tilde{\tau}_{mn}^{af}\langle mn\|ef\rangle \tag{2.3}$$

$$\mathcal{F}_{mi}=(1-\delta_{mi})f_{mi}+\frac{1}{2}\sum_{e}t_i^e f_{me}+\sum_{en}t_n^e\langle mn\|ie\rangle+\frac{1}{2}\sum_{nef}\tilde{\tau}_{in}^{ef}\langle mn\|ef\rangle \tag{2.4}$$

$$\mathcal{F}_{me}=f_{me}+\sum_{nf}t_n^f\langle mn\|ef\rangle \tag{2.5}$$

$$\mathcal{W}_{mnij}=\langle mn\|ij\rangle+P(ij)\sum_{e}t_j^e\langle mn\|ie\rangle+\frac{1}{4}\sum_{ef}\tau_{ij}^{ef}\langle mn\|ef\rangle \tag{2.6}$$

$$\mathcal{W}_{abef}=\langle ab\|ef\rangle-P(ab)\sum_{m}t_m^b\langle am\|ef\rangle+\frac{1}{4}\sum_{mn}\tau_{mn}^{ab}\langle mn\|ef\rangle \tag{2.7}$$

$$\mathcal{W}_{mbej}=\langle mb\|ef\rangle+\sum_{f}t_j^f\langle mb\|ef\rangle-\sum_{n}t_n^b\langle mn\|ej\rangle-\sum_{nf}\left(\frac{1}{2}t_{jn}^{fb}+t_j^f t_n^b\right)\langle mn\|ef\rangle \tag{2.8}$$

Definition of the effective two-particle excitation operators τ and $\tilde{\tau}$:

$$\tilde{\tau}_{ij}^{ab}=t_{ij}^{ab}+\frac{1}{2}\left(t_i^a t_j^b-t_i^b t_j^a\right) \tag{2.9}$$

$$\tau_{ij}^{ab}=t_{ij}^{ab}+t_i^a t_j^b-t_i^b t_j^a \tag{2.10}$$

In the above equations, δ_{pq} is the Kronecker delta, the denominator arrays (D) are defined by

$$D_i^a = f_{ii} - f_{aa} \tag{2.11}$$

and

$$D_{ij}^{ab} = f_{ii} + f_{jj} - f_{aa} - f_{bb} \tag{2.12}$$

and $P(ij)$ and $P(ab)$ are antisymmetric operators given by

$$P(pq) = 1 - \mathcal{P}(pq) \tag{2.13}$$

where $\mathcal{P}(pq)$ interchanges the indices p and q. If we are using a Hartree-Fock reference function, then the diagonal elements of the Fock matrix are simply the orbital eigenvalues. It is important to note that this places the diagonal pieces of f on the left hand side of the equations; this means the diagonal parts of f_{ea} and f_{mi} are excluded from the definition of the corresponding $\mathcal{F}$ intermediates.

At this point, we can now extract the terms which are required to obtain the correct solution for each order of ROHF-MBPT. In order to get the terms, we make the choice that f_{ia} is a first order term, while f_{ab} and f_{ij} are zeroth order terms. With this in mind, we look at the total order of each of the contributing terms. The expressions for the first order amplitudes are therefore

$$t_i^{a(1)} D_i^a = f_{ia} + \sum_e t_i^{e(1)} \mathcal{F}_{ae}^{(0)} - \sum_m t_m^{a\ (1)} \mathcal{F}_{mi}^{(0)} \tag{2.14}$$

$$t_{ij}^{ab(1)} D_{ij}^{ab} = \langle ij \| ab \rangle + P(ab) \sum_e t_{ij}^{ae(1)} \mathcal{F}_{be}^{(0)} - P(ij) \sum_m t_{im}^{ab\ (1)} \mathcal{F}_{mj}^{(0)} \tag{2.15}$$

The expressions for the second order amplitudes are

$$t_i^{a(2)} D_i^a = \sum_e t_i^{e(2)} \mathcal{F}_{ae}^{(0)} - \sum_m t_m^{a\ (2)} \mathcal{F}_{mi}^{(0)}$$

$$+\sum_{me} t_{im}^{ae\,(1)}\mathcal{F}_{me}^{(1)} - \sum_{nf} t_n^{f\,(1)}\langle na\|if\rangle - \frac{1}{2}\sum_{mef} t_{im}^{ef\,(1)}\langle ma\|ef\rangle$$

$$-\frac{1}{2}\sum_{men} t_{mn}^{ae\,(1)}\langle nm\|ei\rangle \tag{2.16}$$

$$\begin{aligned} t_{ij}^{ab(2)}D_{ij}^{ab} &= P(ab)\sum_e t_{ij}^{ae(2)}\mathcal{F}_{be}^{(0)} - P(ij)\sum_m t_{im}^{ab\,(2)}\mathcal{F}_{mj}^{(0)} \\ &+ \frac{1}{2}\sum_{mn}\tau_{mn}^{ab\,(1)}\mathcal{W}_{mnij}^{(1)} + \frac{1}{2}\sum_{ef}\tau_{ij}^{ef(1)}\mathcal{W}_{abef}^{(1)} \\ &+ P(ij)P(ab)\sum_{me} t_{im}^{ae\,(1)}\mathcal{W}_{mbej}^{(1)} + P(ij)\sum_e t_i^{e(1)}\langle ab\|ej\rangle \\ &- P(ab)\sum_m t_m^{a\,(1)}\langle mb\|ij\rangle \end{aligned} \tag{2.17}$$

The expressions for the third order amplitudes (neglecting triple excitations) are

$$\begin{aligned} t_i^{a(3)}D_i^a &= \sum_e \left(t_i^{e(3)}\mathcal{F}_{ae}^{(0)} + t_i^{e(1)}\mathcal{F}_{ae}^{(2)}\right) \\ &- \sum_m \left(t_m^{a\,(3)}\mathcal{F}_{mi}^{(0)} + t_m^{a\,(1)}\mathcal{F}_{mi}^{(2)}\right) \\ &+ \sum_{me} \left(t_{im}^{ae\,(2)}\mathcal{F}_{me}^{(1)} + t_{im}^{ae\,(1)}\mathcal{F}_{me}^{(2)}\right) \\ &- \sum_{nf} t_n^{f\,(2)}\langle na\|if\rangle - \frac{1}{2}\sum_{mef} t_{im}^{ef\,(2)}\langle ma\|ef\rangle \\ &- \frac{1}{2}\sum_{men} t_{mn}^{ae\,(2)}\langle nm\|ei\rangle \end{aligned} \tag{2.18}$$

$$\begin{aligned} t_{ij}^{ab(3)}D_{ij}^{ab} &= P(ab)\sum_e \left(t_{ij}^{ae(3)}\mathcal{F}_{be}^{(0)} + t_{ij}^{ae(1)}\mathcal{F}_{be}^{(2)}\right) \\ &- \frac{1}{2}P(ab)\sum_e t_{ij}^{ae(1)}\sum_m t_m^{b\,(1)}\mathcal{F}_{me}^{(1)} \end{aligned}$$

$$
\begin{aligned}
&- P(ij)\sum_m \left(t_{im}^{ab\,(3)} \mathcal{F}_{mj}^{(0)} + t_{im}^{ab\,(1)} \mathcal{F}_{mj}^{(2)} \right) \\
&- \frac{1}{2} P(ij) \sum_m t_{im}^{ab\,(1)} \sum_e t_j^{e(1)} \mathcal{F}_{me}^{(1)} \\
&+ \frac{1}{2} \sum_{mn} \left(\tau_{mn}^{ab\,(2)} \mathcal{W}_{mnij}^{(1)} + \tau_{mn}^{ab\,(1)} \mathcal{W}_{mnij}^{(2)} \right) \\
&+ \frac{1}{2} \sum_{ef} \left(\tau_{ij}^{ef\,(2)} \mathcal{W}_{abef}^{(1)} + \tau_{ij}^{ef\,(1)} \mathcal{W}_{abef}^{(2)} \right) \\
&+ P(ij)P(ab) \sum_{me} \left(\left[t_{im}^{ae\,(2)} \mathcal{W}_{mbej}^{(1)} + t_{im}^{ae\,(1)} \mathcal{W}_{mbej}^{(2)} \right] - t_i^{e(1)} t_m^{a\,(1)} \langle mb \| ej \rangle \right) \\
&+ P(ij) \sum_e t_i^{e(2)} \langle ab \| ej \rangle - P(ab) \sum_m t_m^{a\,(2)} \langle mb \| ij \rangle
\end{aligned}
\tag{2.19}
$$

If we have a Hartree-Fock reference function, then the $\mathcal{F}^{(0)}$ intermediates are all zero, since the Fock matrix is diagonal. However, the α and β Fock matrices formed from the ROHF eigenvectors are not diagonal, and so the $F^{(0)}$ intermediates are nonzero. For this reason each of the amplitudes must be solved for by iterating until they do not change.

A more efficient approach is obtained by exploiting the invariance of the MBPT energy to rotations among the occupied-occupied and virtual-virtual blocks of the Fock matrix. We can use a unitary transformation to rotate the ROHF eigenvectors so that they will now bring the occupied-occupied and virtual-virtual blocks of the Fock matrix to diagonal form. The orbitals which have this property are called semicanonical orbitals [30]. This transformation does not change the character of the occupied-virtual part of the Fock matrix, however. These blocks of the Fock matrix still have nonzero elements. However, their values are changed to reflect the use of the new orbitals.

Using semicanonical orbitals we can express the T amplitudes as

First order amplitudes:

$$t_i^{a(1)} D_i^a = f_{ia} \tag{2.20}$$

$$t_{ij}^{ab(1)} D_{ij}^{ab} = \langle ij \| ab \rangle \tag{2.21}$$

Second order amplitudes:

$$\begin{aligned} t_i^{a(2)} D_i^a &= \sum_{me} t_{im}^{ae\,(1)} \mathcal{F}_{me}^{(1)} - \sum_{nf} t_n^{f\,(1)} \langle na \| if \rangle - \frac{1}{2} \sum_{mef} t_{im}^{ef\,(1)} \langle ma \| ef \rangle \\ &\quad - \frac{1}{2} \sum_{men} t_{mn}^{ae\,(1)} \langle nm \| ei \rangle \end{aligned} \tag{2.22}$$

$$\begin{aligned} t_{ij}^{ab(2)} D_{ij}^{ab} &= \frac{1}{2} \sum_{mn} \tau_{mn}^{ab\,(1)} \mathcal{W}_{mnij}^{(1)} + \frac{1}{2} \sum_{ef} \tau_{ij}^{ef\,(1)} \mathcal{W}_{abef}^{(1)} \\ &\quad + P(ij) P(ab) \sum_{me} t_{im}^{ae\,(1)} \mathcal{W}_{mbej}^{(1)} \\ &\quad + P(ij) \sum_{e} t_i^{e(1)} \langle ab \| ej \rangle - P(ab) \sum_{m} t_m^{a\,(1)} \langle mb \| ij \rangle \end{aligned} \tag{2.23}$$

Third order amplitudes:

$$\begin{aligned} t_i^{a(3)} D_i^a &= \sum_{e} t_i^{e(1)} \mathcal{F}_{ae}^{(2)} - \sum_{m} t_m^{a\,(1)} \mathcal{F}_{mi}^{(2)} \\ &\quad + \sum_{me} \left(t_{im}^{ae\,(2)} \mathcal{F}_{me}^{(1)} + t_{im}^{ae\,(1)} \mathcal{F}_{me}^{(2)} \right) \\ &\quad - \sum_{nf} t_n^{f(2)} \langle na \| if \rangle - \frac{1}{2} \sum_{mef} t_{im}^{ef\,(2)} \langle ma \| ef \rangle \\ &\quad - \frac{1}{2} \sum_{men} t_{mn}^{ae\,(2)} \langle nm \| ei \rangle \end{aligned} \tag{2.24}$$

$$
\begin{aligned}
t_{ij}^{ab\,(3)} D_{ij}^{ab} \;=\; & P(ab) \sum_e t_{ij}^{ae\,(1)} \mathcal{F}_{be}^{(2)} - \frac{1}{2} P(ab) \sum_e t_{ij}^{ae\,(1)} \sum_m t_m^{b\,(1)} \mathcal{F}_{me}^{(1)} \\
& - P(ij) \sum_m t_{im}^{ab\,(1)} \mathcal{F}_{mj}^{(2)} - \frac{1}{2} P(ij) \sum_m t_{im}^{ab\,(1)} \sum_e t_j^{e\,(1)} \mathcal{F}_{me}^{(1)} \\
& + \frac{1}{2} \sum_{mn} \left(\tau_{mn}^{ab\,(2)} \mathcal{W}_{mnij}^{(1)} + \tau_{mn}^{ab\,(1)} \mathcal{W}_{mnij}^{(2)} \right) \\
& + \frac{1}{2} \sum_{ef} \left(\tau_{ij}^{ef\,(2)} \mathcal{W}_{abef}^{(1)} + \tau_{ij}^{ef\,(1)} \mathcal{W}_{abef}^{(2)} \right) \\
& + P(ij) P(ab) \sum_{me} \left(\left[t_{im}^{ae\,(2)} \mathcal{W}_{mbej}^{(1)} + t_{im}^{ae\,(1)} \mathcal{W}_{mbej}^{(2)} \right] - t_i^{e\,(1)} t_m^{a\,(1)} \langle mb \| ej \rangle \right) \\
& + P(ij) \sum_e t_i^{e\,(2)} \langle ab \| ej \rangle - P(ab) \sum_m t_m^{a\,(2)} \langle mb \| ij \rangle
\end{aligned}
\tag{2.25}
$$

These amplitudes no longer depend on themselves and hence correspond to a non-iterative solution.

In order to get the expressions for the full fourth order energy, we need to examine the contribution of triple excitations. The second order T_3 is given by

$$
\begin{aligned}
t_{ijk}^{abc\,(2)} D_{ijk}^{abc} \;=\; & P(ij/k) P(a/bc) \sum_e t_{ij}^{ae\,(1)} \langle bc \| ek \rangle - P(i/jk) P(ab/c) \sum_m t_{im}^{ab\,(1)} \langle mc \| jk \rangle \\
& + P(ab/c) \sum_e t_{ijk}^{abe\,(2)} f_{ce} - P(ij/k) \sum_m t_{ijm}^{abc\,(2)} f_{mk}
\end{aligned}
\tag{2.26}
$$

In Eqn. (2.26), the operators $P(pq/r)$ mean that p and q may be permuted with r, but not with themselves.[1] Similarly, for $P(p/qr)$, p may be permuted with q or r, but not q and r with themselves. The sign change associated with these operators is given by $(-1)^z$, where z is the number of interchanges. For example, $P(pq/r)$ is represented as

[1] The $P(pq)$ operators defined for the CCSD equations given earlier can be expressed as $P(p/q)$. The slash is dropped since it is redundant; if no interchange occurred, then the operator would be unity and could be omitted from the equations.

$$P(pq/r) = 1 - \mathcal{P}(pr) - \mathcal{P}(qr) \tag{2.27}$$

where $\mathcal{P}$ is the interchange operator defined earlier.

Once again we see that if we use the standard canonical orbitals, we will have to iterate to get $T_3^{(2)}$. For T_3, this requires two additional N^7 contractions and is particularly expensive. Use of standard orbitals would essentially prohibit a full MBPT(4) energy calculation except for a small number of basis functions. However, using semicanonical orbitals eliminates the terms involving contractions with f_{ce} and f_{mk}. This simplifies the expression to

$$t_{ijk}^{abc(2)} D_{ijk}^{abc} = P(ij/k)P(a/bc) \sum_e t_{ij}^{ae(1)} \langle bc \| ek \rangle - P(i/jk)P(ab/c) \sum_m t_{im}^{ab\ (1)} \langle mc \| jk \rangle \tag{2.28}$$

The additional terms arising from inclusion of T_3 in the T_1 and T_2 equations are

$$\Delta t_i^{a(3)} D_i^a = \frac{1}{4} \sum_{mnef} t_{imn}^{aef\ (2)} \langle mn \| ef \rangle \tag{2.29}$$

$$\Delta t_{ij}^{ab(3)} D_{ij}^{ab} = P(ab) \sum_{mef} t_{ijm}^{aef\ (2)} \langle mb \| ef \rangle - P(ij) \sum_{men} t_{imn}^{abe\ (2)} \langle mn \| ej \rangle \tag{2.30}$$

These increments to $T_1^{(3)}$ and $T_2^{(3)}$ are the same as those obtained with a Hartree-Fock reference function.

At this point, we can calculate the MBPT(n) energy using the expression

$$\Delta E^{(n)} = \sum_{ia} t_i^{a(n-1)} f_{ai} + \frac{1}{4} \sum_{ijab} \tau_{ij}^{ab(n-1)} \langle ij \| ab \rangle \tag{2.31}$$

where n is the order of perturbation theory. A more efficient approach to calculating the energy can be realized by exploiting the 2n rule of perturbation theory [31, 32]. This allows the computation of the SDQ-MBPT(4) and full MBPT(4) energies without using the full third order amplitudes. The fourth-order energy contributions

arising from pieces of the third-order amplitudes formed via contractions of $T_1^{(2)}$ and $T_2^{(2)}$ with $\mathcal{F}$ and $\mathcal{W}$ intermediates are given by

$$\begin{aligned}\Delta E_L^{(4)} &= \sum_{ai}\left[t_i^{a(2)}\right]^2 D_i^a + \sum_{abij}\left[t_{ij}^{ab(2)}\right]^2 D_{ij}^{ab} + \sum_{\substack{abc\\ijk}}\left[t_{ijk}^{abc(2)}\right] D_{ijk}^{abc} \\ &\quad + P(ij)P(ab)\sum_{abij} f_{bj}\left[t_i^{a(1)} t_{ij}^{ab(2)} - t_i^{a(2)} t_{ij}^{ab(1)}\right] \end{aligned} \tag{2.32}$$

where "L" stands for linear contributions. Exclusion of the $T_3^{(2)}$ term in Eqn. (2.32) gives the $\Delta E_L^{(4)}$ expression for SDQ-MBPT(4). If we eliminate these linear contributions from the equations for $T_1^{(3)}$ and $T_2^{(3)}$, we need only compute those pieces which are quadratic in the first-order amplitudes. The remaining pieces of the third-order amplitudes are then

$$t_{i\,NL}^{a(3)} D_i^a = \sum_e t_i^{e(1)} \mathcal{F}_{ae}^{(2)} - \sum_m t_m^{a\,(1)} \mathcal{F}_{mi}^{(2)} + \sum_{me} t_{im}^{ae\,(1)} \mathcal{F}_{me}^{(2)} \tag{2.33}$$

$$\begin{aligned} t_{ij\,NL}^{ab(3)} D_{ij}^{ab} &= P(ab)\sum_e t_{ij}^{ae(1)}\left(\mathcal{F}_{be}^{(2)} - \frac{1}{2}\sum_m t_m^{b\,(1)} \mathcal{F}_{me}^{(1)}\right) \\ &\quad - P(ij)\sum_m t_{im}^{ab\,(1)}\left(\mathcal{F}_{mj}^{(2)} + \frac{1}{2}\sum_e t_j^{e(1)} \mathcal{F}_{me}^{(1)}\right) \\ &\quad + \frac{1}{2}\sum_{mn} \tau_{mn}^{ab\,(1)} \mathcal{W}_{mnij}^{(2)} + \frac{1}{2}\sum_{ef} \tau_{ij}^{ef(1)} \mathcal{W}_{abef}^{(2)} \\ &\quad + P(ij)P(ab)\sum_{me}\left(t_{im}^{ae\,(1)} \mathcal{W}_{mbej}^{(2)} - t_i^{e(1)} t_m^{a\,(1)} \langle mb\|ej\rangle\right) \\ &\quad + \frac{1}{2}\sum_{mn} t_m^{a\,(1)} t_n^{b\,(1)} \mathcal{W}_{mnij}^{(1)} + \frac{1}{2}\sum_{ef} t_i^{e(1)} t_j^{f(1)} \mathcal{W}_{abef}^{(1)} \end{aligned} \tag{2.34}$$

where the "NL" means non-linear. It is important to note that the second-order amplitudes do not appear in Eqns. (2.33) and (2.34). The equivalence of these energy expressions is shown in detail in Appendix A, where an analogous algebraic derivation of ROHF-MBPT energies is presented.

The expressions for the semicanonical orbital representation of the amplitudes were programmed through full MBPT(4). Those for the standard orbital representation were programmed through SDQ-MBPT(4) (fourth order without inclusion of triples). This was done to provide a check on the programming of the semicanonical expressions. For several test cases the energies through SDQ-MBPT(4) were in agreement to nine decimal places between the two different orbital representations. This check ensured that our implementation was correct. These methods have now been included in the ACES II [33] program system. Results from calculations using these expressions are given in Chapter 4.

CHAPTER 3
ROHF-MBPT GRADIENTS

The development of gradients for a theoretical method is important if the method is to be routinely applied to chemistry. Searching the potential energy surface of polyatomic systems is generally an intractable problem without ready availability of gradients. Therefore, in conjunction with the development of ROHF-MBPT energies, we also present the theory for ROHF-MBPT gradients through full MBPT(4).

In general, the derivative of the energy can be given by

$$\frac{\partial E\left[c(\chi), C(\chi), I(\chi)\right]}{\partial \chi} = \frac{\partial E}{\partial c}\frac{\partial c}{\partial \chi} + \frac{\partial E}{\partial C}\frac{\partial C}{\partial \chi} + \frac{\partial E}{\partial I}\frac{\partial I}{\partial \chi} \tag{3.1}$$

where c represents the molecular orbital coefficients, C the determinantal coefficients, I the one- and two-electron integrals, and χ is the perturbation. For a CC or MBPT method, all of these derivatives are required. If we consider χ to represent nuclear displacements, then this equation suggests that we need to solve for 3N molecular gradients (N = number of atoms). In practice, it is possible to determine $\partial c/\partial \chi$ by using the Z-vector method [34], which replaces the need to solve $\partial c/\partial \chi$ for all χ with the solution of a single, perturbation-independent linear equation. In a completely analogous fashion, the solution of $\partial C/\partial \chi$ (or $\partial T/\partial \chi$) for each χ can be avoided by solving the linear perturbation-independent Λ equations [35]. This particular development is critical, since without this approach, the need to solve 3N CC (MBPT) problems would eliminate CC/MBPT methods as efficient choices for searching potential energy surfaces.

As with the formulation of expressions for calculating the MBPT energies using an ROHF reference, we start from the gradient expressions for coupled cluster theory. The equations which will be used are based on the formalism of Salter, Trucks, and Bartlett [35], as adapted to handle non-Hartree-Fock cases by Gauss, et. al. [27, 36]. As mentioned above, one important step in the analytic evaluation of the CC energy gradient involves the solution of the Λ or "CC response" equation, which completely accounts for the first order response of the coupled cluster amplitudes to an external perturbation. If we let λ_a^i and λ_{ab}^{ij} represent the Λ amplitudes, then their equations are given by [37]

Λ_1 equations:

$$\begin{aligned}
\lambda_a^i D_i^a &= \mathcal{F}_{ia} + \sum_e \lambda_e^i \tilde{\mathcal{F}}_{im} - \sum_m \lambda_a^m \tilde{\mathcal{F}}_{im} + \frac{1}{2}\sum_m \sum_{ef} \lambda_{ef}^{im} \widetilde{\mathcal{W}}_{efam} + \sum_m \sum_e \lambda_e^m \widetilde{\mathcal{W}}_{eima} \\
&\quad - \frac{1}{2}\sum mne \lambda_{ac}^{mn} \widetilde{\mathcal{W}}_{mnie} - \sum_{ef} \mathcal{G}_{ef} \langle ei \| fa \rangle - \sum_{mn} \mathcal{G}_{mn} \langle mi \| na \rangle \\
&\quad + \sum_m \sum_e \left(\sum_f \mathcal{G}_{fe} t_m^f - \sum_n \mathcal{G}_{mn} t_n^e \right) \langle im \| ae \rangle
\end{aligned} \tag{3.2}$$

Λ_2 equations:

$$\begin{aligned}
\lambda_{ab}^{ij} D_{ij}^{ab} &= \langle ij \| ab \rangle + P_-(ab) \sum_e \lambda_{ij}^{ae} \tilde{\mathcal{F}}_{eb} - P_-(ij) \sum_m \lambda_{ab}^{im} \tilde{\mathcal{F}}_{jm} + \frac{1}{2}\sum_{ef} \lambda_{ef}^{ij} \widetilde{\mathcal{W}}_{efab} \\
&\quad + \frac{1}{2}\sum_{mn} \lambda_{ab}^{mn} \widetilde{\mathcal{W}}_{ijmn} + P_-(ij) P_-(ab) \sum_m \sum_e \lambda_{ae}^{im} \widetilde{\mathcal{W}}_{efmb} \\
&\quad + P_-(ab) \sum_e \langle ij \| ae \rangle \left(\mathcal{G}_{be} - \sum_m \lambda_b^m t_m^e \right) \\
&\quad - P_-(ij) \sum_m \langle im \| ab \rangle \left(\mathcal{G}_{mj} + \sum_e \lambda_e^j t_m^e \right) + P_-(ij) P_-(ab) \lambda_i^a \mathcal{F}_{jb}
\end{aligned}$$

$$+ P_-(ij) \sum_e \lambda_e^i \langle ej \| ab \rangle - P_-(ab) \sum_m \lambda_a^m \langle ij \| mb \rangle \tag{3.3}$$

The $\tilde{\mathcal{F}}$ and $\widetilde{\mathcal{W}}$ intermediates are defined by:

$\tilde{\mathcal{F}}$ intermediates:

$$\tilde{\mathcal{F}}_{ea} = \mathcal{F}_{ea} - \frac{1}{2} \sum_m t_m^e \mathcal{F}_{ma} \tag{3.4}$$

$$\tilde{\mathcal{F}}_{im} = \mathcal{F}_{im} + \frac{1}{2} \sum_e t_m^e \mathcal{F}_{ie} \tag{3.5}$$

$\widetilde{\mathcal{W}}$ intermediates:

$$\begin{aligned} \widetilde{\mathcal{W}}_{efab} &= \langle ef \| ab \rangle - P_-(ef) \sum_m t_m^e \langle mf \| ab \rangle + \frac{1}{2} \sum_{mn} \tau_{mn}^{ef} \langle mn \| ab \rangle \\ &= \mathcal{W}_{efab} + \frac{1}{4} \sum_{mn} \tau_{mn}^{ef} \langle mn \| ab \rangle \end{aligned} \tag{3.6}$$

$$\begin{aligned} \widetilde{\mathcal{W}}_{ijmn} &= \langle ij \| mn \rangle + P_-(mn) \sum_e t_m^e \langle ij \| en \rangle + \frac{1}{2} \sum_{ef} \tau_{mn}^{ef} \langle ef \| ij \rangle \\ &= \mathcal{W}_{ijmn} + \frac{1}{4} \sum_{ef} \tau_{mn}^{ef} \langle ef \| ij \rangle \end{aligned} \tag{3.7}$$

$$\begin{aligned} \widetilde{\mathcal{W}}_{ejmb} &= \langle ej \| mb \rangle + \sum_f t_m^f \langle ej \| fb \rangle - \sum_n t_n^e \langle nj \| mb \rangle \\ &\quad + \sum_n \sum_f \left(t_{mn}^{ef} - t_m^f t_n^e \right) \langle nj \| fb \rangle \\ &= \mathcal{W}_{ejmb} + \frac{1}{2} \sum_n \sum_f t_{mn}^{ef} \langle nj \| fb \rangle \end{aligned} \tag{3.8}$$

$$\widetilde{\mathcal{W}}_{iemn} = \langle ie\|mn\rangle - \sum_f \mathcal{F}_{if} t^{ef}_{mn} - \sum_o t^e_o \widetilde{\mathcal{W}}_{iomn} + \frac{1}{2}\sum_{fg}\langle ie\|fg\rangle \tau^{fg}_{mn} + P_-(mn)\sum_f t^f_m \widetilde{\widetilde{\mathcal{W}}}_{iefn} + P_-(mn)\sum_o\sum_f \langle io\|mn\rangle t^{ef}_{no} \tag{3.9}$$

$$\widetilde{\mathcal{W}}_{efam} = \langle ef\|am\rangle + \sum_n \mathcal{F}_{na} t^{ef}_{mn} + \sum_g t^g_m \widetilde{\mathcal{W}}_{efag} + \frac{1}{2}\sum_{no}\langle am\|no\rangle \tau^{ef}_{no} - P_-(ef)\sum_n t^e_n \widetilde{\widetilde{\mathcal{W}}}_{nfam} + P_-(ef)\sum_n\sum_g \langle en\|ag\rangle t^{fg}_{mn} \tag{3.10}$$

with $\widetilde{\widetilde{\mathcal{W}}}$ given as

$$\widetilde{\widetilde{\mathcal{W}}}_{mbej} = \langle mb\|ej\rangle - \sum_n\sum_f t^{bf}_{nj}\langle mn\|ef\rangle \tag{3.11}$$

For computational reasons, it turns out to be beneficial to define the G intermediates as

$$\mathcal{G}_{ae} = -\frac{1}{2}\sum_{mn}\sum_f t^{ef}_{mn}\lambda^{mn}_{af} \tag{3.12}$$

$$\mathcal{G}_{mi} = \frac{1}{2}\sum_n\sum_{ef} t^{ef}_{mn}\lambda^{in}_{ef} \tag{3.13}$$

These equations hold for all types of single determinantal reference functions because they explicitly include the non-Hartree-Fock terms. We can therefore follow the same prescription as for the energies and show which terms are needed for the Λ equations of MBPT. In the following equations, we will only be deriving expressions for use with semi-canonical orbitals.

First order Λ_1 and Λ_2 equations:

$$\lambda_a^{i\,(1)} D_i^a = f_{ia} \tag{3.14}$$

$$\lambda_{ab}^{ij\,(1)} = \langle ij \| ab \rangle \tag{3.15}$$

These equations look very familiar since they also define the first order T_1 and T_2 amplitudes.

Second order Λ_1 and Λ_2 equations:

$$\begin{aligned}
\lambda_a^{i\,(2)} &= \sum_{nf} t_n^{f\,(1)} \langle in \| af \rangle + \frac{1}{2} \sum_m \sum_{ef} \lambda_{ef}^{im\,(1)} \widetilde{\mathcal{W}}_{efam}^{(1)} + \sum_m \sum_e \lambda_e^{m\,(1)} \widetilde{\mathcal{W}}_{eima}^{(1)} \\
&\quad - \frac{1}{2} \sum_{mn} \sum_e \lambda_{ae}^{mn\,(1)} \widetilde{\mathcal{W}}_{mnie}^{(1)} \\
&= \sum_{nf} t_n^{f\,(1)} \langle in \| af \rangle + \frac{1}{2} \sum_m \sum_{ef} \lambda_{ef}^{im\,(1)} \langle ef \| am \rangle + \sum_m \sum_e \lambda_e^{m\,(1)} \langle ei \| ma \rangle \\
&\quad - \frac{1}{2} \sum_{mn} \sum_e \lambda_{ae}^{mn\,(1)} \langle mn \| ie \rangle
\end{aligned} \tag{3.16}$$

$$\begin{aligned}
\lambda_{ab}^{ij\,(2)} &= \frac{1}{2} \sum_{ef} \lambda_{ef}^{ij\,(1)} \widetilde{\mathcal{W}}_{efab}^{(1)} + \frac{1}{2} \sum_{mn} \lambda_{ab}^{mn\,(1)} \widetilde{\mathcal{W}}_{ijmn}^{(1)} + P_-(ij) P_-(ab) \sum_m \sum_e \lambda_{ae}^{im\,(1)} \widetilde{\mathcal{W}}_{ejmb}^{(1)} \\
&\quad + P_-(ij) P_-(ab) \lambda_a^{i\,(1)} \mathcal{F}_{jb}^{(1)} + P_-(ij) \sum_e \lambda_e^{i\,(1)} \langle ej \| ab \rangle \\
&\quad - P_-(ab) \sum_m \lambda_a^{m\,(1)} \langle ij \| mb \rangle \\
&= \frac{1}{2} \sum_{ef} \lambda_{ef}^{ij\,(1)} \langle ef \| ab \rangle + \frac{1}{2} \sum_{mn} \lambda_{ab}^{mn\,(1)} \langle ij \| mn \rangle \\
&\quad + P_-(ij) P_-(ab) \sum_m \sum_e \lambda_{ae}^{im\,(1)} \langle ej \| mb \rangle + P_-(ij) P_-(ab) \lambda_a^{i\,(1)} f_{jb} \\
&\quad + P_-(ij) \sum_e \lambda_e^{i\,(1)} \langle ej \| ab \rangle - P_-(ab) \sum_m \lambda_a^{m\,(1)} \langle ij \| mb \rangle
\end{aligned} \tag{3.17}$$

These amplitudes are required to obtain MBPT(3) gradients. If we compare the expressions for $\lambda_1^{(2)}$ and $t_1^{(2)}$, and recalling that $\lambda_1^{(1)} = t_1^{(1)}$, we can see that the following equation holds:

$$\lambda_a^{i\,(2)} = t_i^{a(2)} - \sum_{me} t_{im}^{ae\,(1)} f_{me} + \sum_{nf} t_n^{f(1)} \langle in \| af \rangle \tag{3.18}$$

Similarly, comparing $\lambda_2^{(2)}$ and $t_2^{(2)}$ yields

$$\lambda_{ab}^{ij\,(2)} = t_{ij}^{ab(2)} + P_-(ij) P_-(ab) \lambda_a^{i\,(1)} f_{jb} \tag{3.19}$$

Therefore, for MBPT(3) gradients, we need not iterate the Λ equations, but rather take the second order T amplitudes and add several terms. This will lead to a more efficient method of determining the Λ amplitudes which are needed later. Unfortunately, such a simple solution for the third order Λ amplitudes is not possible due to the order-by-order nature of the problem.

Third order Λ_1 and Λ_2 equations (excluding triples):

$$\begin{aligned}
\lambda_a^{i\,(3)} D_i^a \;=\; & \mathcal{F}_{ia}^{(3)} + \sum_e \lambda_e^{i\,(1)} \widetilde{\mathcal{F}}_{ea}^{(2)} - \sum_m \lambda_a^{m(1)} \widetilde{\mathcal{F}}_{im}^{(2)} + \frac{1}{2} \sum_m \sum_{ef} \Big(\lambda_{ef}^{im(2)} \widetilde{\mathcal{W}}_{efam}^{(1)} \\
& + \lambda_{ef}^{im\,(1)} \widetilde{\mathcal{W}}_{efam}^{(2)} \Big) \\
& \frac{1}{2} \sum_m \sum_e \Big(\lambda_e^{m(2)} \widetilde{\mathcal{W}}_{eima}^{(1)} + \lambda_e^{m(1)} \widetilde{\mathcal{W}}_{eima}^{(2)} \Big) \\
& - \frac{1}{2} \sum_{mn} \sum_e \Big(\lambda_{ae}^{mn(2)} \widetilde{\mathcal{W}}_{mnie}^{(1)} + \lambda_{ae}^{mn(1)} \widetilde{\mathcal{W}}_{mnie}^{(2)} \Big) \\
& - \sum_{ef} \mathcal{G}_{ef}^{(2)} \langle ei \| fa \rangle - \sum_{mn} \mathcal{G}_{mn}^{(2)} \langle mi \| na \rangle
\end{aligned} \tag{3.20}$$

$$\lambda_{ab}^{ij\,(3)} D_{ij}^{ab} \;=\; P_-(ab) \sum_e \lambda_{ae}^{ij\,(1)} \widetilde{\mathcal{F}}_{eb}^{(2)} - P_-(ab) \sum_m \lambda_{ab}^{im\,(1)} \widetilde{\mathcal{F}}_{jm}^{(2)}$$

$$
\begin{aligned}
&+ \frac{1}{2}\sum_{ef}\left(\lambda_{ef}^{ij\,(2)}\widetilde{\mathcal{W}}_{efab}^{(1)} + \lambda_{ef}^{ij\,(1)}\widetilde{\mathcal{W}}_{efab}^{(2)}\right) \\
&+ \frac{1}{2}\sum_{mn}\left(\lambda_{ab}^{mn\,(2)}\widetilde{\mathcal{W}}_{ijmn}^{(1)} + \lambda_{ab}^{mn\,(1)}\widetilde{\mathcal{W}}_{ijmn}^{(2)}\right) \\
&+ P_{-}(ij)P_{-}(ab)\sum_{m}\sum_{e}\left(\lambda_{ae}^{im\,(2)}\widetilde{\mathcal{W}}_{ejmb}^{(1)} + \lambda_{ae}^{im\,(1)}\widetilde{\mathcal{W}}_{ejmb}^{(2)}\right) \\
&+ P_{-}(ab)\sum_{e}\langle ij\|ae\rangle\left(\mathcal{G}_{be}^{(2)} - \sum_{m}\lambda_{b}^{m\,(1)}t_{m}^{e\,(1)}\right) \\
&- P_{-}(ij)\sum_{m}\langle im\|ab\rangle\left(\mathcal{G}_{mj}^{(2)} + \sum_{e}\lambda_{e}^{j\,(1)}t_{m}^{e\,(1)}\right) \\
&+ P_{-}(ij)P_{-}(ab)\left(\lambda_{a}^{i\,(2)}\mathcal{F}_{jb}^{(1)} + \lambda_{a}^{i\,(1)}\mathcal{F}_{jb}^{(2)}\right) \\
&+ P_{-}(ij)\sum_{e}\lambda_{e}^{i\,(2)}\langle ej\|ab\rangle - P_{-}(ab)\sum_{m}\lambda_{a}^{m\,(2)}\langle ij\|mb\rangle
\end{aligned}
\tag{3.21}
$$

Since we now have expressions for the t and λ amplitudes obtained from the solution of the CCSD and Λ equations, respectively, we can write the CCSD energy gradient with respect to an external perturbation as

$$
\frac{dE}{d\chi} = \sum_{pq} D_{pq} f_{pq}^{(\chi)} + \sum_{pq} I_{pq} S_{pq}^{\chi} + \sum_{pqrs} \Gamma(pq,rs)\langle pq\|rs\rangle^{\chi} \tag{3.22}
$$

with D_{pq} as the relaxed density, $\Gamma(pq,rs)$ as the effective two-particle density, and I_{pq} as the one-particle intermediate which maintains the orthonormality of the perturbed orbitals. In this expression, the only pieces which depend on the perturbation are the one- and two-electron integrals. These are the derivative AO integrals rotated to the MO basis. Furthermore, it is advantageous to define $f_{pq}^{(\chi)}$ as

$$
f_{pq}^{(\chi)} = h_{pq}^{\chi} + \sum_{m}\langle pm\|qm\rangle^{\chi} \tag{3.23}
$$

which depend only on the AO derivative integrals. The MO derivative part of f_{pq}^{χ} is accounted for in the formation of the relaxed density. The occupied-occupied and

virtual-virtual blocks of the relaxed density are given by

$$D_{ij} = -\frac{1}{4}P_+(ij)\sum_m\sum_{ef} t_{im}^{ef}\lambda_{ef}^{jm} - \frac{1}{2}P_+(ij)\sum_e t_i^e\lambda_e^j \tag{3.24}$$

$$D_{ab} = \frac{1}{4}P_+(ab)\sum_{mn}\sum_e t_{mn}^{ae}\lambda_{be}^{mn} + \frac{1}{2}P_+(ab)\sum_m t_m^a\lambda_b^m \tag{3.25}$$

which constitute the only contributions for Hartree-Fock reference functions. However, for non-Hartree-Fock references, such as ROHF, we also have a contribution to the occupied-virtual block of the relaxed density due to the response of the CC amplitudes

$$\begin{aligned} D_{ai} &= \frac{1}{2}t_i^a + \frac{1}{2}\lambda_a^i + \frac{1}{2}\sum_{me} t_{im}^{ae}\lambda_e^m - \frac{1}{2}\sum_{me} t_m^a t_i^e\lambda_e^m \\ &\quad -\frac{1}{4}\sum_{mn}\sum_{ef}\lambda_{ef}^{mn}t_{in}^{ef}t_m^a - \frac{1}{4}\sum_{mn}\sum_{ef}\lambda_{ef}^{mn}t_{mn}^{af}t_i^e \end{aligned} \tag{3.26}$$

Evaluating each of the D_{pq} terms in an order-by-order fashion gives us the expressions at each level of MBPT. Recall from our discussion of the ROHF-MBPT energies that f_{ij} and f_{ab} are considered zeroth order while f_{ai} is first order. This applies to the derivatives of these elements as well. Therefore, D_{ai} will always be of order $(n-1)$ while D_{ij} or D_{ab} will be of order n, where n is the order of MBPT.

D_{pq} for MBPT(2):

$$\begin{aligned} D_{ij}^{(2)} &= -\frac{1}{4}P_+(ij)\sum_m\sum_{ef} t_{im}^{ae\,(1)}\lambda_{ef}^{jm\,(1)} - \frac{1}{2}P_+(ij)\sum_e t_i^{e(1)}\lambda_e^{j(1)} \\ &= -\frac{1}{4}P_+(ij)\sum_m\sum_{ef} t_{im}^{ae\,(1)}t_{jm}^{ef\,(1)} - \frac{1}{2}P_+(ij)\sum_e t_i^{e(1)}t_e^{j(1)} \end{aligned} \tag{3.27}$$

$$\begin{aligned} D_{ab}^{(2)} &= \frac{1}{4}P_+(ab)\sum_{mn}\sum_e t_{mn}^{ae\ (1)}\lambda_{be}^{mn(1)} + \frac{1}{2}P_+(ab)\sum_m t_m^{a\ (1)}\lambda_b^{m(1)} \\ &= \frac{1}{4}P_+(ab)\sum_{mn}\sum_e t_{mn}^{ae\ (1)}t_{mn}^{be\ (1)} + \frac{1}{2}P_+(ab)\sum_m t_m^{a\ (1)}t_m^{b\ (1)} \end{aligned} \tag{3.28}$$

$$
\begin{aligned}
D_{ai}^{(1)} &= \frac{1}{2} t_i^{a\,(1)} + \frac{1}{2} \lambda_a^{i\,(1)} \\
&= t_i^{a\,(1)} \qquad (3.29)
\end{aligned}
$$

D_{pq} for MBPT(3):

$$
\begin{aligned}
D_{ij}^{(3)} &= -\frac{1}{4} P_+(ij) \sum_m \sum_{ef} \left(t_{im}^{ae\,(2)} \lambda_{ef}^{jm\,(1)} + t_{im}^{ae\,(1)} \lambda_{ef}^{jm\,(2)} \right) \\
&\quad -\frac{1}{2} P_+(ij) \sum_e \left(t_i^{e\,(2)} \lambda_e^{j\,(1)} + t_i^{e\,(1)} \lambda_e^{j\,(2)} \right) \\
&= -\frac{1}{4} P_+(ij) \sum_m \sum_{ef} \left(t_{im}^{ae\,(2)} t_{jm}^{ef\,(1)} + t_{im}^{ae\,(1)} \lambda_{ef}^{jm\,(2)} \right) \\
&\quad -\frac{1}{2} P_+(ij) \sum_e \left(t_i^{e\,(2)} t_j^{e\,(1)} + t_i^{e\,(1)} \lambda_e^{j\,(2)} \right) \qquad (3.30)
\end{aligned}
$$

$$
\begin{aligned}
D_{ab}^{(3)} &= \frac{1}{4} P_+(ab) \sum_{mn} \sum_e \left(t_{mn}^{ae\,(2)} \lambda_{be}^{mn\,(1)} + t_{mn}^{ae\,(1)} \lambda_{be}^{mn\,(2)} \right) \\
&\quad + \frac{1}{2} P_+(ab) \sum_m \left(t_m^{a\,(2)} \lambda_b^{m\,(1)} + t_m^{a\,(1)} \lambda_b^{m\,(2)} \right) \\
&= \frac{1}{4} P_+(ab) \sum_{mn} \sum_e \left(t_{mn}^{ae\,(2)} t_{mn}^{be\,(1)} + t_{mn}^{ae\,(1)} \lambda_{be}^{mn\,(2)} \right) \\
&\quad + \frac{1}{2} P_+(ab) \sum_m \left(t_m^{a\,(2)} t_m^{b\,(1)} + t_m^{a\,(1)} \lambda_b^{m\,(2)} \right) \qquad (3.31)
\end{aligned}
$$

$$
\begin{aligned}
D_{ai}^{(2)} &= \frac{1}{2} t_i^{a\,(2)} + \frac{1}{2} \lambda_a^{i\,(2)} + \frac{1}{2} \sum_{me} t_{im}^{ae\,(1)} \lambda_e^{m\,(1)} \\
&= \frac{1}{2} t_i^{a\,(2)} + \frac{1}{2} \lambda_a^{i\,(2)} + \frac{1}{2} \sum_{me} t_{im}^{ae\,(1)} t_m^{e\,(1)} \qquad (3.32)
\end{aligned}
$$

D_{pq} for SDQ-MBPT(4):

$$
\begin{aligned}
D_{ij}^{(4)} &= -\frac{1}{4} P_+(ij) \sum_m \sum_{ef} \left(t_{im}^{ae\,(3)} \lambda_{ef}^{jm\,(1)} + t_{im}^{ae\,(2)} \lambda_{ef}^{jm\,(2)} + t_{im}^{ae\,(1)} \lambda_{ef}^{jm\,(3)} \right) \\
&\quad -\frac{1}{2} P_+(ij) \sum_e \left(t_i^{e\,(3)} \lambda_e^{j\,(1)} + t_i^{e\,(2)} \lambda_e^{j\,(2)} + t_i^{e\,(1)} \lambda_e^{j\,(3)} \right)
\end{aligned}
$$

$$
\begin{aligned}
&= -\frac{1}{4}P_+(ij)\sum_m\sum_{ef}\left(t_{im}^{ae\,(3)}t_{jm}^{ef\,(1)} + t_{im}^{ae\,(2)}\lambda_{ef}^{jm(2)} + t_{im}^{ae\,(1)}\lambda_{ef}^{jm(3)}\right)\\
&\quad -\frac{1}{2}P_+(ij)\sum_e\left(t_i^{e(3)}t_j^{e(1)} + t_i^{e(2)}\lambda_e^{j(2)} + t_i^{e(1)}\lambda_e^{j(3)}\right) \qquad (3.33)\\
D_{ab}^{(4)} &= \frac{1}{4}P_+(ab)\sum_{mn}\sum_e\left(t_{mn}^{ae\ (3)}\lambda_{be}^{mn(1)} + t_{mn}^{ae\ (2)}\lambda_{be}^{mn(2)} + t_{mn}^{ae\ (1)}\lambda_{be}^{mn(3)}\right)\\
&\quad +\frac{1}{2}P_+(ab)\sum_m\left(t_m^{a\ (3)}\lambda_b^{m(1)} + t_m^{a\ (2)}\lambda_b^{m(2)} + t_m^{a\ (1)}\lambda_b^{m(3)}\right)\\
&= \frac{1}{4}P_+(ab)\sum_{mn}\sum_e\left(t_{mn}^{ae\ (3)}t_{mn}^{be\ (1)} + t_{mn}^{ae\ (2)}\lambda_{be}^{mn(2)} + t_{mn}^{ae\ (1)}\lambda_{be}^{mn(3)}\right)\\
&\quad +\frac{1}{2}P_+(ab)\sum_m\left(t_m^{a\ (3)}t_m^{b\ (1)} + t_m^{a\ (2)}\lambda_b^{m(2)} + t_m^{a\ (1)}\lambda_b^{m(3)}\right) \qquad (3.34)\\
D_{ai}^{(3)} &= \frac{1}{2}t_i^{a(3)} + \frac{1}{2}\lambda_a^{i\ (3)} + \frac{1}{2}\sum_{me}\left(t_{im}^{ae\ (2)}\lambda_e^{m(1)} + t_{im}^{ae\ (1)}\lambda_e^{m(2)}\right)\\
&\quad -\frac{1}{2}\sum_{me}t_m^{a\ (1)}t_i^{e(1)}\lambda_e^{m(1)} - \frac{1}{4}\sum_{mn}\sum_{ef}\lambda_{ef}^{mn(1)}t_{in}^{ef(1)}t_m^{a\ (1)}\\
&\quad -\frac{1}{4}\sum_{mn}\sum_{ef}\lambda_{ef}^{mn(1)}t_{mn}^{af\ (1)}t_j^{e(1)}\\
&= \frac{1}{2}t_i^{a(3)} + \frac{1}{2}\lambda_a^{i\ (3)} + \frac{1}{2}\sum_{me}\left(t_{im}^{ae\ (2)}t_m^{e\ (1)} + t_{im}^{ae\ (1)}\lambda_e^{m(2)}\right)\\
&\quad -\frac{1}{2}\sum_{me}t_m^{a\ (1)}t_i^{e(1)}t_m^{e\ (1)} - \frac{1}{4}\sum_{mn}\sum_{ef}t_{mn}^{ef\ (1)}t_{in}^{ef(1)}t_m^{a\ (1)}\\
&\quad -\frac{1}{4}\sum_{mn}\sum_{ef}t_{mn}^{ef\ (1)}t_{mn}^{af\ (1)}t_j^{e(1)} \qquad (3.35)
\end{aligned}
$$

In all of the above expressions, the first-order λ's have been substituted with the equivalent first-order t amplitudes after giving each expression with the λ's.

The intermediate I'_{pq}, which is a precursor of I_{pq}, is given by

$$I'_{pq} = -\frac{1}{2}\left(\sum_r f_{pr}\left(D_{rq} + D_{qr}\right)\right.$$

$$+\sum_{rst}[\langle pr\|st\rangle\Gamma(qr,st)+\langle rp\|st\rangle\Gamma(rq,st)+\langle rs\|pt\rangle\Gamma(rs,qt)$$

$$+\langle rs\|tp\rangle\Gamma(rs,tq)])-\sum_{rs}\langle pr\|qs\rangle D_{rs}\delta_{qi} \tag{3.36}$$

which is generalized to account for the non-Hartree-Fock nature of the ROHF reference.

In addition to these terms, we need to account for the contribution to the gradient arising from orbital response. This contribution can be obtained by solving the ROHF coupled-perturbed HF (CPHF) equations [38]. For a correlated gradient calculation, however, the CPHF equations are never actually solved, but are replaced with the Z-vector equations [34]. The solution to these equations is added to D to form the full relaxed density.

With $D_{PQ}^{(orb-resp)}$ as the contribution due to orbital response, these equations are given by

$$\sum_E\sum_M D_{EM}^{(orb-resp)}\left(A_{EMAI}^{\alpha\alpha\alpha\alpha}+A_{EMAI}^{\alpha\alpha\beta\beta}+A_{EMAI}^{\beta\beta\alpha\alpha}+A_{EMAI}^{\beta\beta\beta\beta}\right)$$

$$+\sum_E\sum_2 D_{E2}^{(orb-resp)}\left(A_{E2AI}^{\alpha\alpha\alpha\alpha}+A_{E2AI}^{\alpha\alpha\beta\beta}\right)$$

$$+\sum_2\sum_M D_{2M}^{(orb-resp)}\left(A_{2MAI}^{\beta\beta\alpha\beta}+A_{2MAI}^{\beta\beta\beta\beta}\right)=-{}^{\alpha}X_{AI}-{}^{\beta}X_{AI} \tag{3.37}$$

$$\sum_E\sum_M D_{EM}^{(orb-resp)}\left(A_{EMA1}^{\alpha\alpha\alpha\alpha}+A_{EMA1}^{\beta\beta\alpha\alpha}\right)+\sum_E\sum_2 D_{E2}^{(orb-resp)}A_{E2A1}^{\alpha\alpha\alpha\alpha}$$

$$+\sum_2\sum_M D_{2M}^{(orb-resp)}A_{2MA1}^{\beta\beta\alpha\alpha}=-{}^{\alpha}X_{A1} \tag{3.38}$$

$$\sum_E\sum_M D_{EM}^{(orb-resp)}\left(A_{EM1I}^{\alpha\alpha\beta\beta}+A_{EM1I}^{\beta\beta\beta\beta}\right)+\sum_E\sum_2 D_{E2}^{(orb-resp)}A_{E21I}^{\alpha\alpha\beta\beta}$$

$$+\sum_2\sum_M D_{2M}^{(orb-resp)}A_{2M1I}^{\beta\beta\beta\beta}=-{}^{\beta}X_{1I} \tag{3.39}$$

where $I,J,K,\ldots$ refer to doubly occupied orbitals, $A,B,C,\ldots$ refer to virtual orbitals, and $1,2,\ldots$ refer to open-shell (singly occupied) orbitals. The A matrix used in Eqns.

(3.37) to (3.39) are defined as

$$A^{\alpha\alpha\alpha\alpha}_{PQRS} = 2\langle PR|QS\rangle - \langle PR|SQ\rangle - \langle PS|RQ\rangle + \delta_{QS}{}^{\alpha} f_{PR} - \delta_{PR}{}^{\alpha} f_{QS} \quad (3.40)$$

$$A^{\beta\beta\beta\beta}_{PQRS} = 2\langle PR|QS\rangle - \langle PR|SQ\rangle - \langle PS|RQ\rangle + \delta_{QS}{}^{\beta} f_{PR} - \delta_{PR}{}^{\beta} f_{QS} \quad (3.41)$$

$$A^{\alpha\alpha\beta\beta}_{PQRS} = 2\langle PR|QS\rangle + \delta_{QR}{}^{\beta} f_{PS} \quad (3.42)$$

A derivation of these A matrix terms is given in Appendix B. These A matrix elements differ from those for UHF in that various pieces of the α and β Fock matrices need to be included.

Before progressing further, we must discuss the implications of the above expressons on the use of semicanonical orbitals. These expressions have all been developed in the canonical (standard) orbital basis. This was necessary since the partitioning of the orbital space into doubly, singly, and unoccupied orbitals is only true for the canonical orbitals. Rotating the orbitals to the semicanonical orbital basis effectively mixes all the subspaces so that a clear partitioning is no longer possible.

The problem, therefore, is how to solve the CPHF equations if we are in the semicanonical representation. Let us have

$$AU^{X} = B \quad (3.43)$$

represent the general matrix expression for the occupied-virtual part of the CPHF equations using semicanonical orbitals. The occupied-occupied and virtual-virtual parts can be constructed from existing quantities and knowledge of the occupied-virtual part. Multiplying both sides by $Z = XA^{-1}$, we can rewrite Eqn. (3.43) as

$$XU^{X} = ZB \quad (3.44)$$

By solving for Z we can avoid explicitly solving for U^{X}. For the elements of the A matrix which consist only of integrals, we can use the integrals in the semicanonical basis. Of course, to form the product Z of X and A^{-1}, X also needs to be in the

semicanonical basis. However, the addition of the Fock matrix elements must be done in the canonical (standard) basis, since this is where the partitioning of the orbital space is defined. For the product of X with these pieces, X is rotated to the canonical basis

$$\tilde{X} = LXL^{\dagger} \tag{3.45}$$

where L is the unitary matrix which rotated the orbitals from the standard to semicanonical orbital basis and $\tilde{X}$ represents X in the standard orbital basis. After forming the increment Z product between $\tilde{X}$ and the f pieces of the A matrix, this increment is rotated back to the semicanonical basis. Therefore, in practice, we have separated the A matrix into two pieces: the integral part and the Fock matrix part. Additionally, we are able to solve the Z-vector equations without having to perform a complete four-index transformation of the A matrix back to the standard orbital basis. This transformation has been replaced by two-index transformations performed at the appropriate times.

The X_{ai} intermediates are given by

$$X_{ai} = I'_{ia} - I'_{ai} \tag{3.46}$$

The X_{ai} intermediates are only defined for non-redundant orbital rotations among virtual and occupied spin-orbitals. Because of the nature of the ROHF reference, the rotations among singly and doubly occupied orbitals need only be considered for β spin-orbitals, and rotations among singly and unoccupied (virtual) orbitals only for α spin-orbitals. After solving the ROHF-CPHF equations, we have the last contribution to D_{ai}. This allows us to complete the construction of the I_{pq} intermediates

$$I_{ij} = I'_{ij} - 2\sum_{e}\sum_{m} D_{em}^{(orb-resp)}\langle ei\|mj\rangle - 2\sum_{e} f_{ei} D_{ej}^{(orb-resp)}\delta_{j1} \tag{3.47}$$

$$I_{ai} = I_{ia} = I'_{ia} - \sum_{m} f_{im} D_{ma}^{(orb-resp)} \tag{3.48}$$

$$I_{ab} = I'_{ab} \tag{3.49}$$

The last term in I_{ij} is only considered when j corresponds to an open-shell (singly occupied) orbitals, as shown by δ_{j1}.

Elements of the effective two-particle density matrix Γ, which are the coefficients of the derivative two-electron integrals, are given by:

$$\Gamma(ab,cd) = \frac{1}{8}P_+(ab,cd)\mathcal{V}_{abcd} \tag{3.50}$$

$$\Gamma(ij,kl) = \frac{1}{8}P_+(ij,kl)\mathcal{V}_{ijkl} \tag{3.51}$$

$$\Gamma(ib,ja) = \frac{1}{4}P_+(ia,jb)\mathcal{V}_{ibja} + \frac{1}{8}P_+(ia,jb)\sum_m\sum_e t_i^e t_m^a \lambda_{be}^{jm} - \frac{1}{8}P_+(ia,jb)t_i^a\lambda_b^j \tag{3.52}$$

$$\begin{aligned}\Gamma(ij,ab) &= \frac{1}{8}\tau_{ij}^{ab} + \frac{1}{8}\lambda_{ij}^{ab} + \frac{1}{16}\sum_{mn}\tau_{mn}^{ab}\mathcal{V}_{ijmn} - \frac{1}{8}P_-(ij)\sum_m \tau_{mn}^{ab}\left(\mathcal{G}_{im} + \sum_e \lambda_e^m t_i^e\right) \\ &+\frac{1}{8}P_-(ab)\sum_e \tau_{ij}^{eb}\left(\mathcal{G}_{ea} - \sum_m \lambda_e^m t_m^a\right) \\ &-\frac{1}{8}P_-(ij)P_-(ab)\sum_m\sum_e [t_{mi}^{ae} + 2t_m^a t_i^e]\left[\mathcal{V}_{jemb} + \lambda_e^m t_j^b\right] \\ &+\frac{3}{2}P_-(ij)P_-(ab)\sum_m\sum_e t_m^b t_j^e \lambda_e^m t_i^a\end{aligned} \tag{3.53}$$

$$\begin{aligned}\Gamma(ij,ka) &= -\frac{1}{8}\sum_e \lambda_e^k \tau_{ij}^{ea} - \frac{1}{8}\sum_e t_k^e \lambda_{ea}^{ij} + \frac{1}{8}\sum_m \mathcal{V}_{ijkm}t_m^a \\ &+\frac{1}{4}P_-(ij)\sum_f \mathcal{V}_{kfia}t_j^f - \frac{1}{8}P_-(ij)\mathcal{G}_{ik}t_j^a\end{aligned} \tag{3.54}$$

$$\begin{aligned}\Gamma(ab,ci) &= \frac{1}{8}\sum_m \lambda_c^m \tau_{mi}^{ab} + \frac{1}{8}\sum_m t_m^c \lambda_{ab}^{mi} - \frac{1}{8}\sum_e \mathcal{V}_{ceab}t_i^e \\ &+\frac{1}{4}P_-(ab)\sum_m \mathcal{V}_{meia}t_m^a - \frac{1}{8}P_-(ab)\mathcal{G}_{ca}t_i^b\end{aligned} \tag{3.55}$$

with the V intermediates defined by

$$\mathcal{V}_{mnij} = \frac{1}{2}\sum_{ef} \tau_{mn}^{ef} \lambda_{ef}^{ij} \tag{3.56}$$

$$\mathcal{V}_{abef} = \frac{1}{2}\sum_{mn} \tau_{mn}^{ef} \lambda_{ab}^{mn} \tag{3.57}$$

$$\mathcal{V}_{ibja} = \frac{1}{2}\sum_{m}\sum_{e} t_{im}^{ae} \lambda_{be}^{jm} \tag{3.58}$$

As with the CC and Λ equations, we must evaluate each of these two-particle density matrix terms order-by-order. Before writing down each of the terms for each order of MBPT, note that the $\mathcal{G}$ and $\mathcal{V}$ intermediates are a minimum of second order.

Γ intermediates for MBPT(2):

$$\Gamma^{(1)}(ij,ab) = \frac{1}{8}\tau_{ij}^{ab(1)} + \frac{1}{8}\lambda_{ab}^{ij\,(1)} \tag{3.59}$$

Γ intermediates for MBPT(3):

$$\Gamma^{(2)}(ab,cd) = \frac{1}{8}P_+(ab,cd)\mathcal{V}_{abcd}^{(2)} \tag{3.60}$$

$$\Gamma^{(2)}(ij,kl) = \frac{1}{8}P_+(ij,kl)\mathcal{V}_{ijkl}^{(2)} \tag{3.61}$$

$$\Gamma^{(2)}(ib,ja) = \frac{1}{4}P_+(ia,jb)\mathcal{V}_{ibja}^{(2)} + \frac{1}{8}P_+(ia,jb)t_i^{a(1)}\lambda_b^{j(1)} \tag{3.62}$$

$$\Gamma^{(2)}(ij,ab) = \frac{1}{8}\tau_{ij}^{ab(2)} + \frac{1}{8}\lambda_{ab}^{ij\,(2)} \tag{3.63}$$

$$\Gamma^{(2)}(ij,ka) = -\frac{1}{8}\sum_{e}\lambda_e^{k(1)}\tau_{ij}^{ea(1)} - \frac{1}{8}\sum_{e} t_k^{e\,(1)}\lambda_{ea}^{ij\,(1)} \tag{3.64}$$

$$\Gamma^{(2)}(ab,ci) = \frac{1}{8}\sum_{m}\lambda_e^{m(1)}t_{mi}^{ab\,(1)} + \frac{1}{8}\sum_{m} t_m^{e\,(1)}\lambda_{ab}^{mi(1)} \tag{3.65}$$

Γ intermediates for SDQ-MBPT(4):

$$\Gamma^{(3)}(ab,cd) = \frac{1}{8}P_+(ab,cd)\mathcal{V}^{(3)}_{abcd} \tag{3.66}$$

$$\Gamma^{(3)}(ij,kl) = \frac{1}{8}P_+(ij,kl)\mathcal{V}^{(3)}_{ijkl} \tag{3.67}$$

$$\begin{aligned}\Gamma^{(3)}(ib,ja) = {} & \frac{1}{4}P_+(ia,jb)\mathcal{V}^{(3)}_{ibja} + \frac{1}{8}P_+(ia,jb)\sum_m\sum_e t^{e\,(1)}_i t^{a\,(1)}_m \lambda^{jm\,(1)}_{be} \\ & -\frac{1}{8}P_+(ia,jb)\left[t^{a\,(2)}_i\lambda^{j\,(1)}_b + t^{a\,(1)}_i\lambda^{j\,(2)}_b\right]\end{aligned} \tag{3.68}$$

$$\begin{aligned}\Gamma^{(3)}(ij,ab) = {} & \frac{1}{8}\tau^{ab\,(3)}_{ij} + \frac{1}{8}\lambda^{ij\,(3)}_{ab} + \frac{1}{16}\sum_{mn}\tau^{ab\,(1)}_{mn}\mathcal{V}^{(2)}_{ijmn} \\ & -\frac{1}{8}P_-(ij)\sum_m \tau^{ab\,(1)}_{mj}\left(\mathcal{G}^{(2)}_{im} + \sum_e \lambda^{m\,(1)}_e t^{e\,(1)}_i\right) \\ & +\frac{1}{8}P_-(ab)\sum_e \tau^{eb\,(1)}_{ij}\left(\mathcal{G}^{(2)}_{ea} - \sum_m \lambda^{m\,(1)}_e t^{a\,(1)}_m\right) \\ & -\frac{1}{8}P_-(ij)P_-(ab)\sum_m\sum_e t^{ae\,(1)}_{mi}\left(\mathcal{V}^{(2)}_{jemb} + \lambda^{m\,(1)}_e t^{b\,(1)}_j\right)\end{aligned} \tag{3.69}$$

$$\begin{aligned}\Gamma^{(3)}(ij,ka) = {} & -\frac{1}{8}\sum_e\left(\lambda^{k\,(2)}_e\tau^{ea\,(1)}_{ij} + \lambda^{k\,(1)}_e\tau^{ea\,(2)}_{ij}\right) \\ & -\frac{1}{8}\sum_e\left(t^{e\,(2)}_k\lambda^{ij\,(1)}_{ea} + t^{e\,(1)}_k\lambda^{ij\,(2)}_{ea}\right) \\ & +\frac{1}{8}\sum_m \mathcal{V}^{(2)}_{ijkm}t^{a\,(1)}_m + \frac{1}{4}P_-(ij)\sum_f \mathcal{V}^{(2)}_{kfia}t^{f\,(1)}_j \\ & -\frac{1}{8}P_-(ij)\mathcal{G}^{(2)}_{ik}t^{a\,(1)}_j\end{aligned} \tag{3.70}$$

$$\begin{aligned}\Gamma^{(3)}(ab,ci) = {} & \frac{1}{8}\sum_m\left(\lambda^{m\,(2)}_c\tau^{ab\,(1)}_{mi} + \lambda^{m\,(1)}_c\tau^{ab\,(2)}_{mi}\right) \\ & +\frac{1}{8}\sum_m\left(t^{c\,(2)}_m\lambda^{mi\,(1)}_{ab} + t^{c\,(1)}_m\lambda^{mi\,(2)}_{ab}\right) \\ & +\frac{1}{8}\sum_e \mathcal{V}^{(2)}_{ceab}t^{e\,(1)}_i + \frac{1}{4}P_-(ij)\sum_f \mathcal{V}^{(2)}_{meia}t^{a\,(1)}_m\end{aligned}$$

$$-\frac{1}{8}P_{-}(ab)\mathcal{G}_{ca}^{(2)}t_{i}^{b(1)} \tag{3.71}$$

In order to have gradients for full fourth-order, we need to include the contributions from T_3 and also Λ_3. The expression for Λ_3 which is correct through MBPT(4) is

$$\begin{aligned}\lambda_{abc}^{ijk(2)}D_{ijk}^{abc} &= P(a/bc)P(ij/k)\sum_{e}\lambda_{ae}^{ij\,(1)}\langle ek\|bc\rangle - P(ab/c)P(i/jk)\sum_{m}\lambda_{ab}^{im\,(1)}\langle jk\|mc\rangle \\ &\quad + P(a/bc)P(i/jk)\lambda_{a}^{i\,(1)}\langle jk\|bc\rangle + P(ab/c)P(ij/k)\lambda_{ab}^{ij\,(1)}f_{ck}\end{aligned} \tag{3.72}$$

Recognizing some similar pieces between the expression between $\Lambda_3^{(2)}$ and $T_3^{(2)}$ we can simplify to

$$\begin{aligned}\lambda_{abc}^{ijk(2)}D_{ijk}^{abc} &= t_{ijk}^{abc(2)} + P(a/bc)P(i/jk)\lambda_{a}^{i\,(1)}\langle jk\|bc\rangle + P(ab/c)P(ij/k)\lambda_{ab}^{ij\,(1)}f_{ck} \\ &= t_{ijk}^{abc(2)} + P(a/bc)P(i/jk)t_{a}^{i\,(1)}\langle jk\|bc\rangle + P(ab/c)P(ij/k)t_{ab}^{ij\,(1)}f_{ck}\end{aligned} \tag{3.73}$$

where we have also used the equivalence between the first-order t's and λ's. The inclusion of triple excitations also leads to the following additional terms for the relaxed density

$$D_{ij}^{(4)}(triples) = -\frac{1}{24}\sum_{efg}\sum_{mn}\lambda_{abc}^{jik(2)}t_{lki}^{abc(2)} \tag{3.74}$$

$$D_{ab}^{(4)}(triples) = \frac{1}{24}\sum_{ef}\sum_{mno}\lambda_{aef}^{mno(2)}t_{mno}^{bef\,(2)} \tag{3.75}$$

$$\begin{aligned}D_{ai}^{(3)}(triples) &= \frac{1}{4}\sum_{mn}\sum_{ef}\left(\lambda_{efa}^{mni(2)}t_{mn}^{ef\,(1)} + \lambda_{ef}^{mn(1)}t_{mni}^{efa\,(2)}\right) \\ &= \frac{1}{4}\sum_{mn}\sum_{ef}\left(\lambda_{efa}^{mni(2)}t_{mn}^{ef\,(1)} + t_{ef}^{mn(1)}t_{mni}^{efa\,(2)}\right)\end{aligned} \tag{3.76}$$

Additional terms also arise for some of the Γ intermediates. Specifically

$$\Gamma^{(3)}(ij,ab)(triples) = \frac{1}{4}\sum_{em}\lambda_e^{m\,(1)}t_{mij}^{eab\,(2)}$$

$$= \frac{1}{4}\sum_{em}t_m^{e\,(1)}t_{mij}^{eab\,(2)} \tag{3.77}$$

$$\Gamma^{(3)}(ij,ka)(triples) = \frac{1}{4}\sum_{ef}\sum_{m}\left(\lambda_{ef}^{im\,(1)}t_{mjk}^{efa\,(2)} - \lambda_{aef}^{jkm\,(2)}t_{mi}^{ef\,(1)}\right)$$

$$= \frac{1}{4}\sum_{ef}\sum_{m}\left(t_{im}^{ef\,(1)}t_{mjk}^{efa\,(2)} - \lambda_{aef}^{jkm\,(2)}t_{mi}^{ef\,(1)}\right) \tag{3.78}$$

$$\Gamma^{(3)}(ab,ci)(triples) = \frac{1}{4}\sum_{e}\sum_{mn}\left(\lambda_{ebc}^{mni\,(2)}t_{mn}^{ae\,(1)} - \lambda_{ae}^{mn\,(1)}t_{mni}^{ebc\,(2)}\right)$$

$$= \frac{1}{4}\sum_{e}\sum_{mn}\left(\lambda_{ebc}^{mni\,(2)}t_{mn}^{ae\,(1)} - t_{mn}^{ae\,(1)}t_{mni}^{ebc\,(2)}\right) \tag{3.79}$$

Programming of these terms, in addition to the appropriate CPHF terms for ROHF (derived in Appendix B), allow the analytic calculation of the energy gradient. Since these equations are derived from the general CC and Λ expressions, including the non-Hartree-Fock terms, the additional pieces from the CPHF allow the direct implementation of the ROHF-CCSD gradients, which have been published elsewhere [27]. The gradients for MBPT(2), MBPT(3), and CCSD are implemented in the ACES II [33] *ab initio* program system.

CHAPTER 4

RESULTS OF ROHF-MBPT CALCULATIONS

In order to gain an understanding of how the ROHF-MBPT approach works in practice, a number of different atomic and molecular systems are studied. The focus of these studies is to observe how spin contamination (or lack of) in the UHF reference affects the results. It will also be important to see how well ROHF performs on systems which may or may not suffer from spin contamination. In the rest of the chapter, we will examine the following problems:

1. Electron affinities and ionization potentials of first row atoms (B-F).

2. Structure and characterization of several spin contaminated diatomic and polyatomic molecules:

   (a) CH_2O + H transition state
   (b) CN
   (c) Li_3
   (d) FCS
   (e) N_2H

4.1 Atomic Calculations

One of the first things we wish to examine is the difference between UHF and ROHF for determining the electron affinities and first ionization potentials of the first row atoms. To this end, we use three basis sets of increasingly better quality. These are the "correlation consistent" basis sets of Dunning [39]. These basis sets follow the progression that as the description of s and p space improves, a corresponding

Table 4.1. UHF atomic energies for the ground state of the first row atoms and their ions using the PVDZ basis set.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)
B^- (^3P)	-24.4991843	-24.5464594	-24.5604404	-24.5643397	-24.5648663
B (^2P)	-24.5299616	-24.5674982	-24.5810576	-24.5861892	-24.5865312
B^+ (^1S)	-24.2345624	-24.2680974	-24.2820318	-24.2885273	-24.2885378
C^- (^4S)	-37.6795011	-37.7482812	-37.7622148	-37.7643165	-37.7648067
C (^3P)	-37.6865444	-37.7396554	-37.7545104	-37.7586740	-37.7591232
C^+ (^2P)	-37.2895279	-37.3321260	-37.3473327	-37.3532686	-37.3535455
N^- (^3P)	-54.2692744	-54.3698640	-54.3836453	-54.3852375	-54.3857122
N (^4S)	-54.3911146	-54.4634378	-54.4769727	-54.4790434	-54.4794748
N^+ (^3P)	-53.8804629	-53.9358715	-53.9508049	-53.9551823	-53.9555518
O^- (^2P)	-74.7211942	-74.8632513	-74.8731035	-74.8741629	-74.8746738
O (^3P)	-74.7921661	-74.8958841	-74.9089220	-74.9104537	-74.9110503
O^+ (^4S)	-74.3524680	-74.4239253	-74.4363601	-74.4383394	-74.4387234
F^- (^1S)	-99.3659836	-99.5566556	-99.5579529	-99.5595439	-99.5601917
F (^2P)	-99.3752403	-99.5177561	-99.5271689	-99.5281917	-99.5290407
F^+ (^3P)	-98.8004853	-98.9007679	-98.9126153	-98.9141213	-98.9147770

[a]SDQ(4) is SDQ-MBPT(4).

increase in the polarization functions should occur. These basis sets are a $[3s2p1d]$ valence double zeta basis (PVDZ), a $[4s3p2d1f]$ valence triple zeta basis (PVTZ), and a $[5s4p3d2f1g]$ valence quadruple zeta basis (PVQZ). All the atomic calculations are performed by using spherical functions, i.e. the cartesian contaminants of the d, f, and g functions are removed. The UHF energies for the first row atoms, and their cations and anions, are shown in Tables 4.1 to 4.3; the ROHF energies are in Tables 4.4 to 4.6. The differences between the atomic energies for the UHF and ROHF references are in Tables 4.7 to 4.9. A comparison of the SCF results for UHF and ROHF shows that the ROHF energies are always higher, which follows because the ROHF reference is a restricted reference and because the lowest unrestricted (UHF) result must be lower or equal in energy by the variational principal. For the energies at the third and both fourth order levels of MBPT, the ROHF energies are all slightly lower, except for F(^{2}P) with the PVDZ and PVQZ basis sets, since no such

Table 4.2. UHF atomic energies for the ground state of the first row atoms and their ions using the PVTZ basis set.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)
B^- (^3P)	-24.5100311	-24.5767271	-24.5911231	-24.5943998	-24.5959395
B (^2P)	-24.5320678	-24.5833893	-24.5964003	-24.6008792	-24.6015718
B^+ (^1S)	-24.2366822	-24.2793439	-24.2918120	-24.2975397	-24.2976287
C^- (^4S)	-37.6961487	-37.7960390	-37.8108438	-37.8121665	-37.8145090
C (^3P)	-37.6915692	-37.7672401	-37.7822139	-37.7856918	-37.7869203
C^+ (^2P)	-37.2947464	-37.3536597	-37.3682976	-37.3734925	-37.3740887
N^- (^3P)	-54.3038136	-54.4529887	-54.4680940	-54.4692338	-54.4724256
N (^4S)	-54.4006862	-54.5068109	-54.5209161	-54.5223322	-54.5240773
N^+ (^3P)	-53.8901742	-53.9713094	-53.9863828	-53.9900874	-53.9910372
O^- (^2P)	-74.7661931	-74.9770178	-74.9865150	-74.9875070	-74.9921297
O (^3P)	-74.8117566	-74.9659719	-74.9804662	-74.9816235	-74.9840964
O^+ (^4S)	-74.3703743	-74.4786578	-74.4918371	-74.4932792	-74.4945240
F^- (^1S)	-99.4242987	-99.7056911	-99.7026464	-99.7053271	-99.7117115
F (^2P)	-99.4055249	-99.6173738	-99.6275244	-99.6283434	-99.6318270
F^+ (^3P)	-98.8302558	-98.9850719	-98.9986662	-98.9998199	-99.0015584

[a]SDQ(4) is SDQ-MBPT(4).

Table 4.3. UHF atomic energies for the ground state of the first row atoms and their ions using the PVQZ basis set.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)
B^- (^3P)	-24.5156480	-24.6013072	-24.6159378	-24.6188769	-24.6209894
B (^2P)	-24.5329671	-24.6013403	-24.6145264	-24.6187957	-24.6196603
B^+ (^1S)	-24.2374671	-24.2960874	-24.3088602	-24.3144339	-24.3146148
C^- (^4S)	-37.7036686	-37.8276158	-37.8423528	-37.8431689	-37.8465328
C (^3P)	-37.6933078	-37.7897908	-37.8047220	-37.8078789	-37.8094339
C^+ (^2P)	-37.2964677	-37.3746496	-37.3894141	-37.3943442	-37.3950945
N^- (^3P)	-54.3177573	-54.4991682	-54.5140060	-54.5146764	-54.5194247
N (^4S)	-54.4037180	-54.5349103	-54.5488291	-54.5498944	-54.5521796
N^+ (^3P)	-53.8931758	-53.9973488	-54.0124015	-54.0157919	-54.0169846
O^- (^2P)	-74.7828574	-75.0353382	-75.0435681	-75.0442597	-75.0513951
O (^3P)	-74.8172947	-75.0037462	-75.0181948	-75.0189823	-75.0222625
O^+ (^4S)	-74.3756476	-74.5108266	-74.5238544	-74.5249742	-74.5265786
F^- (^1S)	-99.4446198	-99.7777376	-99.7719363	-99.7751000	-99.7850545
F (^2P)	-99.4137701	-99.6659486	-99.6761440	-99.6765936	-99.6812561
F^+ (^3P)	-98.8386639	-99.0278311	-99.0415320	-99.0423611	-99.0446002

[a]SDQ(4) is SDQ-MBPT(4).

Table 4.4. ROHF atomic energies for the ground state of the first row atoms and their ions using the PVDZ basis set.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)
B^- (^3P)	-24.4965182	-24.5462395	-24.5605960	-24.5644453	-24.5650042
B (^2P)	-24.5265909	-24.5673461	-24.5814411	-24.5864598	-24.5868398
C^- (^4S)	-37.6786938	-37.7480836	-37.7622496	-37.7643871	-37.7648709
C (^3P)	-37.6824179	-37.7393526	-37.7548043	-37.7588812	-37.7593576
C^+ (^2P)	-37.2855906	-37.3319545	-37.3476953	-37.3535082	-37.3538165
N^- (^3P)	-54.2656755	-54.3700342	-54.3838976	-54.3853091	-54.3858099
N (^4S)	-54.3884142	-54.4631538	-54.4772032	-54.4792130	-54.4796415
N^+ (^3P)	-53.8752649	-53.9355580	-53.9511380	-53.9553884	-53.9557840
O^- (^2P)	-74.7182444	-74.8634416	-74.8732315	-74.8741687	-74.8747018
O (^3P)	-74.7875131	-74.8959359	-74.9091628	-74.9105046	-74.9111211
O^+ (^4S)	-74.3482550	-74.4236688	-74.4366790	-74.4385142	-74.4389005
F (^2P)	-99.3718619	-99.5179134	-99.5272832	-99.5281846	-99.5290511
F^+ (^3P)	-98.7950288	-98.9007937	-98.9128445	-98.9141613	-98.9148338

[a]SDQ(4) is SDQ-MBPT(4).

Table 4.5. ROHF atomic energies for the ground state of the first row atoms and their ions using the PVTZ basis set.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)
B^- (^3P)	-24.5069886	-24.5767131	-24.5913669	-24.5945123	-24.5961324
B (^2P)	-24.5281466	-24.5835479	-24.5969163	-24.6011601	-24.6019312
C^- (^4S)	-37.6950825	-37.7957407	-37.8108646	-37.8122589	-37.8145865
C (^3P)	-37.6867081	-37.7672302	-37.7826183	-37.7859050	-37.7872067
C^+ (^2P)	-37.2902724	-37.3538057	-37.3687486	-37.3737131	-37.3743689
N^- (^3P)	-54.2989075	-54.4534292	-54.4685124	-54.4693451	-54.4726437
N (^4S)	-54.3973578	-54.5066112	-54.5211959	-54.5225128	-54.5242763
N^+ (^3P)	-53.8843449	-53.9713577	-53.9867895	-53.9902651	-53.9912779
O^- (^2P)	-74.7620804	-74.9774746	-74.9867466	-74.9875212	-74.9922332
O (^3P)	-74.8056444	-74.9663199	-74.9808337	-74.9816974	-74.9842602
O^+ (^4S)	-74.3658228	-74.4785794	-74.4921546	-74.4934216	-74.4946972
F (^2P)	-99.4009353	-99.6177769	-99.6277189	-99.6283477	-99.6318999
F^+ (^3P)	-98.8236176	-98.9854452	-98.9989867	-98.9998732	-99.0016813

[a]SDQ(4) is SDQ-MBPT(4).

Table 4.6. ROHF atomic energies for the ground state of the first row atoms and their ions using the PVQZ basis set.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)
B^- (^3P)	-24.5125729	-24.6013588	-24.6161815	-24.6189913	-24.6212011
B (^2P)	-24.5289645	-24.6016581	-24.6150615	-24.6190617	-24.6200218
C^- (^4S)	-37.7022742	-37.8271465	-37.8423651	-37.8433248	-37.8466423
C (^3P)	-37.6882984	-37.7899382	-37.8051540	-37.8080915	-37.8097363
C^+ (^2P)	-37.2919347	-37.3749564	-37.3898206	-37.3945418	-37.3953631
N^- (^3P)	-54.3121834	-54.4997005	-54.5145026	-54.5148154	-54.5197210
N (^4S)	-54.4001759	-54.5347595	-54.5491231	-54.5500897	-54.5523924
N^+ (^3P)	-53.8873215	-53.9975898	-54.0128115	-54.0159462	-54.0172144
O^- (^2P)	-74.7783733	-75.0359181	-75.0438259	-75.0442689	-75.0515426
O (^3P)	-74.8108436	-75.0042248	-75.0185706	-75.0190470	-75.0224441
O^+ (^4S)	-74.3711469	-74.5109057	-74.5241680	-74.5251023	-74.5267424
F (^2P)	-99.4089519	-99.6664597	-99.6763438	-99.6765916	-99.6813461
F^+ (^3P)	-98.8318860	-99.0283812	-99.0418538	-99.0424016	-99.0447278

[a]SDQ(4) is SDQ-MBPT(4).

Table 4.7. Atomic energy differences (E_{UHF} - E_{ROHF}) for the ground state of the first row atoms and their ions using the PVDZ basis set.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)
B^- (^3P)	-0.0026661	-0.0002199	0.0001556	0.0001056	0.0001379
B (^2P)	-0.0033707	-0.0001521	0.0003835	0.0002706	0.0003086
C^- (^4S)	-0.0008073	-0.0001976	0.0000348	0.0000706	0.0000642
C (^3P)	-0.0041265	-0.0003028	0.0002939	0.0002072	0.0002344
C^+ (^2P)	-0.0039373	-0.0001715	0.0003626	0.0002396	0.0002710
N^- (^3P)	-0.0035989	0.0001702	0.0002523	0.0000716	0.0000977
N (^4S)	-0.0027004	-0.0002840	0.0002305	0.0001696	0.0001667
N^+ (^3P)	-0.0051980	-0.0003135	0.0003331	0.0002061	0.0002322
O^- (^2P)	-0.0029498	0.0001903	0.0001280	0.0000058	0.0000280
O (^3P)	-0.0046530	0.0000518	0.0002408	0.0000509	0.0000708
O^+ (^4S)	-0.0042130	-0.0002565	0.0003189	0.0001748	0.0001771
F (^2P)	-0.0033784	0.0001573	0.0001143	-0.0000071	0.0000104
F^+ (^3P)	-0.0054565	0.0000258	0.0002292	0.0000400	0.0000568

[a]SDQ(4) is SDQ-MBPT(4).

Table 4.8. Atomic energy differences (E_{UHF} - E_{ROHF}) for the ground state of the first row atoms and their ions using the PVTZ basis set.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)
B^- (^3P)	-0.0030425	-0.0000140	0.0002438	0.0001125	0.0001929
B (^2P)	-0.0039212	0.0001586	0.0005160	0.0002809	0.0003594
C^- (^4S)	-0.0010662	-0.0002983	0.0000208	0.0000924	0.0000775
C (^3P)	-0.0048611	-0.0000099	0.0004044	0.0002132	0.0002864
C^+ (^2P)	-0.0044740	0.0001460	0.0004510	0.0002206	0.0002802
N^- (^3P)	-0.0049061	0.0004405	0.0004184	0.0001113	0.0002181
N (^4S)	-0.0033284	-0.0001997	0.0002798	0.0001806	0.0001990
N^+ (^3P)	-0.0058293	0.0000483	0.0004067	0.0001777	0.0002407
O^- (^2P)	-0.0041127	0.0004568	0.0002316	0.0000142	0.0001035
O (^3P)	-0.0061122	0.0003480	0.0003675	0.0000739	0.0001638
O^+ (^4S)	-0.0045515	-0.0000784	0.0003175	0.0001424	0.0001732
F (^2P)	-0.0045896	0.0004031	0.0001945	0.0000043	0.0000729
F^+ (^3P)	-0.0066382	0.0003733	0.0003205	0.0000533	0.0001229

[a]SDQ(4) is SDQ-MBPT(4).

Table 4.9. Atomic energy differences (E_{UHF} - E_{ROHF}) for the ground state of the first row atoms and their ions using the PVQZ basis set.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)
B^- (^3P)	-0.0030751	0.0000516	0.0002437	0.0001144	0.0002117
B (^2P)	-0.0040026	0.0003178	0.0005351	0.0002660	0.0003615
C^- (^4S)	-0.0013944	-0.0004693	0.0000123	0.0001559	0.0001095
C (^3P)	-0.0050094	0.0001474	0.0004320	0.0002126	0.0003024
C^+ (^2P)	-0.0045330	0.0003068	0.0004065	0.0001976	0.0002686
N^- (^3P)	-0.0055739	0.0005323	0.0004966	0.0001390	0.0002963
N (^4S)	-0.0035421	-0.0001508	0.0002940	0.0001953	0.0002128
N^+ (^3P)	-0.0058543	0.0002410	0.0004100	0.0001543	0.0002298
O^- (^2P)	-0.0044841	0.0005799	0.0002578	0.0000092	0.0001475
O (^3P)	-0.0064511	0.0004786	0.0003758	0.0000647	0.0001816
O^+ (^4S)	-0.0045007	0.0000791	0.0003136	0.0001281	0.0001638
F (^2P)	-0.0048182	0.0005111	0.0001998	-0.0000020	0.0000900
F^+ (^3P)	-0.0067779	0.0005501	0.0003218	0.0000405	0.0001276

[a]SDQ(4) is SDQ-MBPT(4).

variational primcipal applies for perturbation theory. At the MBPT(2) level, we see that improving the basis causes the ROHF-MBPT(2) energies to become lower than the UHF-MBPT(2) energies. With the PVDZ basis, most of the ROHF-MBPT(2) energies are higher than UHF-MBPT(2). With the PVTZ basis, ROHF-MBPT(2) energies are lower except for B^-, C^-, C, N, and O^+. The PVQZ basis results show that UHF-MBPT(2) energies are lower only for C^- and N. If a larger basis set in this series were available ("PVPZ"), perhaps even these last two atomic systems would be lower for ROHF-MBPT(2).

The differences between these energies give us the electron affinities (EA) and ionization potentials (IP) for the atoms. The ionization potentials using the UHF reference are shown in Table 4.10 while the ROHF results are in Table 4.11. For reference, the experimental values are presented in both tables. The first thing to note is that at the SCF level, the value of the IP is essentially invariant to basis set. This is not surprising since these basis sets have fundamentally the same ability to describe the orbitals in the atomic environment. Compared to experiment, the SCF results are not very good, although the UHF values are generally better, all being higher by 0.01-0.1 eV. Upon introduction of correlation, we see the differences between the basis sets arise. With both UHF and ROHF, the larger basis gives a larger value for each IP. In fact, the UHF and ROHF results now differ by no more than ≈ 0.01 eV. The PVDZ results all underestimate the IP's and are particularly poor for O and F. The PVTZ basis gives excellent agreement for B, C, and N, and improves the results for O and F. The largest basis, PVQZ, actually leads to an overestimation of the IP's for B, C, and N, but further improves the O and F IP's.

Given the different nature of the two references, it is important to understand why they should give essentially the same values for the IP's. This agreement can be best understood by examining the degree of spin contamination in the UHF reference. The

Table 4.10. UHF ionization potentials (electron volts) for the first row atoms using several basis sets.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)	Experiment[b]
PVDZ basis						
B	8.038	8.147	8.137	8.100	8.109	8.298
C	10.803	11.090	11.080	11.032	11.036	11.260
N	13.896	14.356	14.318	14.255	14.257	14.534
O	11.965	12.843	12.859	12.847	12.853	13.618
F	15.640	16.789	16.723	16.710	16.715	17.422
PVTZ basis						
B	8.038	8.274	8.288	8.254	8.271	8.298
C	10.798	11.254	11.263	11.217	11.234	11.260
N	13.892	14.572	14.546	14.483	14.505	14.534
O	12.011	13.261	13.296	13.289	13.322	13.618
F	15.654	17.206	17.112	17.103	17.151	17.422
PVQZ basis						
B	8.041	8.306	8.318	8.282	8.301	8.298
C	10.799	11.297	11.301	11.253	11.275	11.260
N	13.893	14.628	14.597	14.534	14.564	14.534
O	12.018	13.413	13.451	13.443	13.488	13.618
F	15.650	17.364	17.269	17.258	17.324	17.422

[a]SDQ(4) is SDQ-MBPT(4).

[b]Reference [40].

Table 4.11. ROHF ionization potentials (electron volts) for the first row atoms using several basis sets.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)	Experiment[b]
PVDZ basis						
B	7.947	8.143	8.147	8.107	8.117	8.298
C	10.798	11.086	11.078	11.031	11.035	11.260
N	13.964	14.357	14.315	14.254	14.255	14.534
O	11.953	12.851	12.857	12.844	12.850	13.618
F	15.697	16.793	16.720	16.709	16.714	17.422
PVTZ basis						
B	7.931	8.278	8.302	8.262	8.281	8.298
C	10.788	11.250	11.262	11.216	11.234	11.260
N	13.960	14.565	14.542	14.483	14.504	14.534
O	11.968	13.272	13.298	13.287	13.322	13.618
F	15.710	17.207	17.109	17.102	17.149	17.422
PVQZ basis						
B	7.932	8.315	8.332	8.289	8.311	8.298
C	10.786	11.292	11.302	11.253	11.276	11.260
N	13.956	14.617	14.594	14.535	14.563	14.534
O	11.965	13.424	13.453	13.441	13.489	13.618
F	15.703	17.363	17.265	17.257	17.323	17.422

[a]SDQ(4) is SDQ-MBPT(4).
[b]Reference [40].

Table 4.12. UHF spin multiplicities at the SCF and MBPT(2) levels of theory, with three different basis sets.

	SCF			MBPT(2)		
	PVDZ	PVTZ	PVQZ	PVDZ	PVTZ	PVQZ
B^- (^3P)	3.0038559	3.0058750	3.0067849	3.0019841	3.0034223	3.0041740
B (^2P)	2.0074386	2.0103563	2.0111184	2.0039144	2.0060088	2.0066251
B^+ (^1S)	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000
C^- (^4S)	4.0009071	4.0015236	4.0026212	4.0006028	4.0010860	4.0019862
C (^3P)	3.0042068	3.0060185	3.0067453	3.0021681	3.0034322	3.0040167
C^+ (^2P)	2.0054362	2.0065773	2.0066579	2.0026331	2.0034133	2.0034809
N^- (^3P)	3.0028757	3.0058363	3.0093850	3.0014628	3.0035263	3.0063672
N (^4S)	4.0020148	4.0030439	4.0037057	4.0011783	4.0019160	4.0024484
N^+ (^3P)	3.0036957	3.0045905	3.0046566	3.0017814	3.0023880	3.0024623
O^- (^2P)	2.0022867	2.0046215	2.0065766	2.0009847	2.0024349	2.0039108
O (^3P)	3.0029098	3.0047962	3.0056704	3.0014571	3.0026621	3.0033193
O^+ (^4S)	4.0021732	4.0027121	4.0027950	4.0011450	4.0015283	4.0016230
F^- (^1S)	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000
F (^2P)	2.0020049	2.0034116	2.0039139	2.0008289	2.0016005	2.0019395
F^+ (^3P)	3.0024791	3.0033791	3.0035304	3.0011390	3.0016529	3.0017681

average multiplicity[1] at each level of theory with each basis set is given in Tables 4.12 to 4.15. The first and most important thing to note is that the UHF reference is hardly contaminated. This is the principal reason why the UHF and ROHF results are the same. However, there are some interesting things to note about the behavior of the spin contamination. First, as the basis set is improved, the multiplicity worsens. This is contrary what might have been expected, but is not surprising when one considers that the contaminating excited states are better described (that is, have a lower energy) in the larger basis sets, enhancing their contribution to an erroneous multiplicity. Second, the contamination is decreased with every increase in the level of theory. This is generally expected (but cannot be expected rigorously) since further inclusion of correlation provides a better description of the wavefunction, which

[1]It is important to point out how the value for S^2 is determined. Handy, et. al. [20] use a non-variational expectation value expression (Eqn. (30) of reference [20]). McDouall and Schlegel [19] use an expectation value. Our approach is to calculate S^2 via the formula $\langle 0|S^2|\phi^{(n)}\rangle$, where n is the same as for MBPT(n). Details of this formula can be found in reference [13].

Table 4.13. UHF spin multiplicities at the MBPT(3) level of theory, with three different basis sets, with and without inclusion of T_1.

	PVDZ		PVTZ		PVQZ	
	No T_1	With T_1	No T_1	With T_1	No T_1	With T_1
B^- (^3P)	3.0012158	3.0008845	3.0023897	3.0016952	3.0030456	3.0021926
B (^2P)	2.0024497	2.0017654	2.0042387	2.0029277	2.0048434	2.0032741
B^+ (^1S)	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000
C^- (^4S)	4.0004111	4.0003394	4.0007839	4.0006482	4.0014801	4.0012863
C (^3P)	3.0013159	3.0009900	3.0023485	3.0016804	3.0028691	3.0020324
C^+ (^2P)	2.0015479	2.0010980	2.0022519	2.0014874	2.0023661	2.0015018
N^- (^3P)	3.0009856	3.0006872	3.0026453	3.0019469	3.0050781	3.0039394
N (^4S)	4.0007531	4.0006005	4.0013349	4.0010182	4.0017713	4.0013591
N^+ (^3P)	3.0010298	3.0007629	3.0015491	3.0010642	3.0016537	3.0010962
O^- (^2P)	2.0006341	2.0004104	2.0017604	2.0012188	2.0030096	2.0022098
O (^3P)	3.0009340	3.0006921	3.0018710	3.0013741	3.0024260	3.0018076
O^+ (^4S)	4.0006897	4.0005300	4.0010046	4.0007313	4.0011070	4.0007859
F^- (^1S)	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000
F (^2P)	2.0005089	2.0003402	2.0010830	2.0007229	2.0013651	2.0009293
F^+ (^3P)	3.0006838	3.0005014	3.0010848	3.0007476	3.0011993	3.0008102

Table 4.14. UHF spin multiplicities at the SDQ-MBPT(4) level of theory, with three different basis sets, with and without inclusion of T_1.

	PVDZ		PVTZ		PVQZ	
	No T_1	With T_1	No T_1	With T_1	No T_1	With T_1
B^- (^3P)	3.0008994	3.0003643	3.0019171	3.0008269	3.0024940	3.0011806
B (^2P)	2.0018786	2.0007018	2.0034774	2.0013286	2.0040576	2.0015444
B^+ (^1S)	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000
C^- (^4S)	4.0001781	4.0003074	4.0005927	4.0003649	4.0011398	4.0007966
C (^3P)	3.0009710	3.0004196	3.0018584	3.0008014	3.0023282	3.0010291
C^+ (^2P)	2.0011529	2.0004029	2.0018008	2.0006023	2.0019325	2.0006157
N^- (^3P)	3.0007964	3.0003459	3.0022323	3.0011559	3.0043890	3.0025767
N (^4S)	4.0005615	4.0002834	4.0010396	4.0005181	4.0014083	4.0007416
N^+ (^3P)	3.0007453	3.0003020	3.0012037	3.0004623	3.0013169	3.0004897
O^- (^2P)	2.0005134	2.0001975	2.0014885	2.0007022	2.0025943	2.0014054
O (^3P)	3.0007193	3.0003460	3.0015151	3.0007661	3.0019994	3.0010733
O^+ (^4S)	4.0005047	4.0002290	4.0007683	4.0003401	4.0008673	4.0003818
F^- (^1S)	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000
F (^2P)	2.0003974	2.0001589	2.0008884	2.0003821	2.0011360	2.0005255
F^+ (^3P)	3.0005083	3.0002324	3.0008561	3.0003698	3.0009654	3.0004150

Table 4.15. UHF spin multiplicities at the MBPT(4) level of theory, with three different basis sets, with and without inclusion of T_1.

	PVDZ		PVTZ		PVQZ	
	No T_1	With T_1	No T_1	With T_1	No T_1	With T_1
B^- (^3P)	3.0008848	3.0003606	3.0018628	3.0007995	3.0024218	3.0011422
B (^2P)	2.0018544	2.0007012	2.0034132	2.0013125	2.0039766	2.0015239
B^+ (^1S)	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000
C^- (^4S)	4.0001766	4.0003077	4.0005970	4.0003707	4.0008061	4.0011510
C (^3P)	3.0009593	3.0004137	3.0018182	3.0007800	3.0022742	3.0010008
C^+ (^2P)	2.0011382	2.0004022	2.0017663	2.0005934	2.0018910	2.0006041
N^- (^3P)	3.0007822	3.0003394	3.0021698	3.0011232	3.0042786	3.0025133
N (^4S)	4.0005584	4.0002778	4.0010275	4.0005112	4.0013881	4.0007293
N^+ (^3P)	3.0007358	3.0002973	3.0011759	3.0004478	3.0012829	3.0004722
O^- (^2P)	2.0005007	2.0001909	2.0014284	2.0006629	2.0024913	2.0013310
O (^3P)	3.0007079	3.0003369	3.0014686	3.0007336	3.0010239	3.0010239
O^+ (^4S)	4.0004999	4.0002229	4.0007540	4.0003312	4.0008481	4.0003701
F^- (^1S)	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000	1.0000000
F (^2P)	2.0003885	2.0001524	2.0008487	2.0003519	2.0010794	2.0004802
F^+ (^3P)	3.0004998	3.0002243	3.0008265	3.0003481	3.0009280	3.0003878

ultimately has to become an eigenfunction of spin in the limit of full configuration interaction (CI). Third, the effect of including T_1 in determining the multiplicity is relatively significant. For a UHF reference function, the T_1 part of the wavefunction becomes non-zero at MBPT(3). This leads to a further improvement in the multiplicity and is continued at fourth order. From the coupled-cluster viewpoint, it is important to include T_1 in the evaluation of $\hat{S}^2$.

If we now turn our focus to the electron affinities, we see that these basis sets have substantial problems. The electron affinities for the PVDZ, PVTZ, and PVQZ basis sets for both UHF and ROHF are shown in Table 4.16 and Table 4.17, respectively. In general, differences between UHF and ROHF results at the correlated level are not greater than ≈ 0.02 eV, and most often agree to within 0.005 eV. In addition, at the SCF level the ROHF results are better than the UHF results with all the basis sets. Focussing on each basis set in turn, we see that both ROHF and UHF fail to show that any of the atoms have a positive electron affinity at the SCF level with the PVDZ basis. Qualitatively this is only correct for N. The ROHF-SCF EA's, however, are a qualitative improvement over UHF since they give a less negative EA for B, C, O, and F and a larger negative EA for N. In going to the correlated level, both references show improvement. However, even at MBPT(4), the EA's are qualitatively incorrect for both B and O. Moving to the PVTZ basis, the SCF results again parallel those for PVDZ with respect to the UHF/ROHF differences. At the SCF level, there is now qualitative agreement for C, N, and F, while B and O are still incorrect. At the correlated level, we once again see marked improvement over the SCF level. Oxygen is now predicted to have a positive EA. Boron, however, is still qualitatively incorrect. Another important note is that the best quantitative results are given by MBPT(2) rather than MBPT(4). With the PVQZ basis, the SCF results are quantitatively better than PVTZ, but qualitatively the same in that they both fail to predict a positive EA for B and O. At the correlated level, we see again substantial

Table 4.16. UHF electron affinities (electron volts) for the first row atoms using several basis sets.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)	Experiment[b]
PVDZ basis						
B	-0.837	-0.572	-0.561	-0.595	-0.590	0.277
C	-0.192	0.235	0.210	0.154	0.155	1.2629
N	-3.315	-2.546	-2.540	-2.553	-2.551	Not stable
O	-1.931	-0.888	-0.975	-0.988	-0.990	1.461125
F	-0.252	1.059	0.838	0.853	0.848	3.399
PVTZ basis						
B	-0.600	-0.181	-0.144	-0.176	-0.153	0.277
C	0.125	0.784	0.779	0.720	0.751	1.2629
N	-2.636	-1.465	-1.437	-1.445	-1.406	Not stable
O	-1.240	0.301	0.165	0.160	0.219	1.461125
F	0.511	2.403	2.044	2.095	2.174	3.399
PVQZ basis						
B	-0.471	-0.001	0.038	0.002	0.036	0.277
C	0.282	1.029	1.024	0.960	1.010	1.2629
N	-2.339	-0.973	-0.948	-0.958	-0.891	Not stable
O	-0.937	0.860	0.690	0.688	0.793	1.461125
F	0.839	3.042	2.607	2.681	2.825	3.399

[a]SDQ(4) is SDQ-MBPT(4).
[b]Reference [40].

Table 4.17. ROHF electron affinities (electron volts) for the first row atoms using several basis sets.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)	Experiment[b]
PVDZ basis						
B	-0.818	-0.574	-0.567	-0.599	-0.594	0.277
C	-0.101	0.238	0.203	0.150	0.150	1.2629
N	-3.340	-2.534	-2.539	-2.555	-2.553	Not stable
O	-1.885	-0.884	-0.978	-0.989	-0.991	1.461125
F	-0.160	1.054	0.835	0.853	0.847	3.399
PVTZ basis						
B	-0.576	-0.186	-0.151	-0.181	-0.158	0.277
C	0.228	0.776	0.769	0.717	0.745	1.2629
N	-2.679	-1.447	-1.434	-1.447	-1.405	Not stable
O	-1.185	0.304	0.161	0.158	0.217	1.461125
F	0.636	2.392	2.039	2.095	2.172	3.399
PVQZ basis						
B	-0.446	-0.008	0.030	-0.002	0.032	0.277
C	0.380	1.012	1.013	0.959	1.004	1.2629
N	-2.394	-0.954	-0.942	-0.960	-0.889	Not stable
O	-0.884	0.862	0.687	0.686	0.792	1.461125
F	0.971	3.028	2.601	2.681	2.822	3.399

[a]SDQ(4) is SDQ-MBPT(4).
[b]Reference [40].

improvement over the SCF results and at the MBPT(4) level we now have qualitative agreement for all atoms.

The poor performance of these basis sets to quantitatively (and sometimes qualitatively) predict the EA's of B-F can be traced easily to the lack of diffuse functions in the valence space. Each improvement of these basis sets is designed to give better results in a molecular environment where emphasis is placed on effectively describing the regions of space near the nuclei. For determining EA's, however, more emphasis needs to be placed on regions of space further from the nuclei. Dunning and Hay [41] recommend the addition of a single diffuse p function which is found to significantly improve the performance of their DZP basis sets in predicting electron affinities. The recommended p function was added to each of the basis sets to create augmented basis sets termed PVDZ+, PVTZ+, and PVQZ+. These basis sets are used in calculations on the neutral atoms and their anions. In general, we see the same trends in the energies as with the unaugmented basis sets. The exceptions do not follow any particular trend with increasing basis set size. With the PVQZ+ basis set, all the ROHF correlated energies are lower than their UHF counterparts, except for the SDQ-MBPT(4) energy for F (^{2}P). In the PVDZ+ basis, the energies for the N^- (^{3}P) are reversed against the trend of UHF-MBPT energies being lower. The difference between the UHF-MBPT and ROHF-MBPT energies for this anion are also larger than most of the differences. This is due to the poor description which UHF gives for this anion, as reflected by its significant spin contamination (Table 4.18). While the multiplicities with the augmented basis sets follow the same trends as for the unaugmented bases, the N^- result is very different. It is interesting to note that this severe contamination occurred from the addition of a single diffuse p function. This probably follows from the important additional freedom provided by this function which causes a large disparity in the spatial distribution of the α electrons and hence

Table 4.18. UHF multiplicities for N^- at several levels of theory using the PVDZ+, PVTZ+, and PVQZ+ basis sets.

	SCF	MBPT(2)	MBPT(3)	
			No T_1	With T_1
PVDZ+	3.1958594	3.1807852	3.1734463	3.1522835
PVTZ+	3.1817883	3.1671957	3.1605805	3.1366364
PVQZ+	3.1909866	3.1760152	3.1692977	3.1425726
	SDQ(4)[a]		MBPT(4)	
	No T_1	With T_1	No T_1	With T_1
PVDZ+	3.1668339	3.1279970	3.1659764	3.1281129
PVTZ+	3.1549507	3.1118335	3.1539288	3.1119625
PVQZ+	3.1636241	3.1158145	3.1625191	3.1159292

[a]SDQ(4) is SDQ-MBPT(4).

lead to large spin contamination. However, without additional data it is difficult to conclusively ascribe this result to this idea.

The effects of the additional *p* function on the atomic electron affinities can be seen in Tables 4.19 and 4.20. With the PVDZ+ basis, there is now qualitative agreement for C, N, and F at the SCF level, while the PVDZ basis failed for this. As with the PVDZ basis, the ROHF results are different from the UHF results in the direction toward agreement with experiment. With the PVTZ+ and PVQZ+ bases, we see the same qualitative behavior as with their unaugmented counterparts. However, the additional *p* function significantly improves the quantitative agreement. The EA's for C and F are much higher than for the unaugmented bases, with the most gain seen for the PVDZ+ basis. In addition, even though still qualitatively wrong for B and O at the SCF level, the magnitude of the error has been remarkably decreased. Upon introduction of correlation, the EA's come significantly closer to the experimental values. As with the first basis sets, the MBPT(2) results are higher and closer to experiment. The differences between MBPT(2) and MBPT(4) with the augmented bases, however, are about half that of the differences for the unaugmented bases.

Table 4.19. UHF electron affinities for the first row atoms using several basis sets augmented with a single diffuse p function.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)	Experiment[b]
PVDZ+ basis						
B	-0.386	-0.031	0.009	-0.015	-0.001	0.277
C	0.368	0.939	0.934	0.886	0.903	1.2629
N	-1.888	-1.085	-1.070	-1.024	-1.000	Not stable
O	-0.616	0.949	0.706	0.788	0.888	1.461125
F	1.194	3.165	2.637	2.868	3.011	3.399
PVTZ+ basis						
B	-0.348	0.118	0.167	0.137	0.167	0.277
C	0.402	1.143	1.141	1.081	1.125	1.2629
N	-1.861	-0.827	-0.812	-0.759	-0.705	Not stable
O	-0.603	1.231	0.968	1.019	1.165	1.461125
F	1.171	3.442	2.860	3.054	3.259	3.399
PVQZ+ basis						
B	-0.321	0.184	0.231	0.196	0.236	0.277
C	0.430	1.233	1.227	1.162	1.222	1.2629
N	-1.835	-0.714	-0.695	-0.635	-0.565	Not stable
O	-0.592	1.385	1.122	1.159	1.333	1.461125
F	1.168	3.599	3.011	3.185	3.425	3.399

[a]SDQ(4) is SDQ-MBPT(4).
[b]Reference [40].

Table 4.20. ROHF electron affinities for the first row atoms using several basis sets augmented with a single diffuse p function.

	SCF	MBPT(2)	MBPT(3)	SDQ(4)[a]	MBPT(4)	Experiment[b]
PVDZ+ basis						
B	-0.345	-0.028	0.005	-0.017	-0.003	0.277
C	0.465	0.942	0.927	0.882	0.898	1.2629
N	-2.097	-0.909	-0.925	-0.905	-0.848	Not stable
O	-0.587	0.945	0.695	0.785	0.888	1.461125
F	1.288	3.162	2.635	2.869	3.012	3.399
PVTZ+ basis						
B	-0.307	0.115	0.160	0.134	0.164	0.277
C	0.511	1.134	1.130	1.078	1.119	1.2629
N	-2.048	-0.603	-0.619	-0.619	-0.530	Not stable
O	-0.563	1.230	0.961	1.017	1.166	1.461125
F	1.297	3.432	2.855	3.054	3.257	3.399
PVQZ+ basis						
B	-0.282	0.178	0.224	0.194	0.234	0.277
C	0.535	1.216	1.216	1.161	1.217	1.2629
N	-2.030	-0.449	-0.463	-0.473	-0.363	Not stable
O	-0.552	1.386	1.118	1.158	1.335	1.461125
F	1.300	3.586	3.006	3.185	3.422	3.399

[a]SDQ(4) is SDQ-MBPT(4).
[b]Reference [40].

The conclusion which can be drawn from these atomic calculations is that no significant differences exist between use of the UHF or ROHF references. This can be anticipated by noting that the UHF reference has essentially no spin contamination. The significant errors between experimental and calculated electron affinities can be directly connected to the basis set. Even a small improvement in the basis (addition of a single diffuse p function) leads to a drastic improvement in the computed EA's.

4.2 The CH_2O + H transition state

The addition of hydrogen to formaldehyde is a reaction which has been studied by McDouall and Schlegel [19] using projected MBPT(2), i.e. MP2 (PMP2) gradient methods, which eliminate the first (quartet) contaminant. In this work, we examined the geometry of the transition state at the MBPT(2) level of theory. These results, and the corresponding PMP2 results, are shown in Table 4.21. We see that the geometries for all three methods are similar. The barrier height for this reaction is not known experimentally, so we shall use the ROHF-CCSD result as our figure of merit. The UHF-MBPT(2) barrier height is 27.0 kcal/mol (11.2 kcal/mol above the ROHF-CCSD result), while the PMPn[1] result of McDouall and Schlegel improves the UHF-MBPT(2) result fairly well, reducing the barrier height to 22.2 kcal/mol. The ROHF-MBPT(2) result is better still, yielding a barrier of 19.2 kcal/mol, only 3.4 kcal/mol above the ROHF-CCSD result. The is further improved as one goes to higher levels of perturbation theory, with the full MBPT(4) result only 1.8 kcal/mol above our best estimate. It is interesting to note that inclusion of triples at MBPT(4) causes

[1]The PMPn energy is determined at the PMP2 geometry with all contaminants eliminated. The barrier height reported in [19] used the frozen core MP2 energy for the CH_2O fragment and the all-electron MP2 energy for the transition state. The barrier reported here corrects this error; Schlegel, H. B., personal communication, June 1991.

Table 4.21. Geometry and barrier heights for the transition state of the CH_2O + H $\rightarrow$ CH_2OH addition reaction using the 6-31G* basis set.

	UHF-MBPT(2)	PMP2	ROHF-MBPT(2)
Structure[a]			
R(C-O)	1.230	1.249	1.260
R(C-H)	1.097	1.096	1.096
R(O-H)	1.422	1.464	1.422
θ(H-C-H)	116.63	117.38	117.67
θ(H-O-C)	120.93	118.51	119.59
θ(X-C-O)	177.31	176.66	176.53
Barrier(kcal/mole)[b]			
	UHF	PMPn	ROHF
MBPT(2)	27.0	22.2	19.2
MBPT(3)	21.8		18.8
SDQ-MBPT(4)	21.5		18.0
MBPT(4)	23.3		17.6
CCSD	16.1		15.8

[a]Bond lengths are in Angstroms; angles are in degrees.

[b]All barrier heights were determined using the optimized MBPT(2) geometries.

Table 4.22. Optimized geometries[a] for CN and CN^- using the PVDZ and PVTZ basis sets and UHF multiplicities.

	PVDZ			PVTZ		
	SCF	MBPT(2)	CCSD	SCF	MBPT(2)	CCSD
CN^- (RHF)	1.162	1.204	1.192	1.151	1.184	1.171
CN (UHF)	1.162	1.138	1.183	1.150	1.123	1.163
CN (ROHF)	1.139	1.210	1.184	1.129	1.187	1.164
UHF multiplicity	2.337	2.233	2.043	2.302	2.201	2.041

[a]Bond lengths are in Å.

the barrier to rise for UHF, while for ROHF the barrier continues to decrease. ROHF-MBPT provides an improved result over PMP2 for this system at the MBPT(2) level and also provides improved energies at higher orders of MBPT.

4.3 The Cyano (CN) Radical

This radical has long been known to be spin contaminated and identified as a failure of UHF based MBPT [42]. For this reason, it provides an excellent example for comparing ROHF and UHF based MBPT methods. The geometry of CN was optimized at the SCF, MBPT(2), and CCSD levels using the PVDZ and PVTZ basis sets. The UHF and ROHF geometries of CN, along with those for CN^-, are given in Table 4.22. Looking at only the PVDZ results, we see that in going from SCF to MBPT(2), the UHF bond length contracts by 0.024 Å. This is contrary to what is expected, since it is well known that MBPT(2) tends to overestimate the effect of correlation on bond lengths [43]. The ROHF bond, however, lengthens in going from SCF to MBPT(2), which is in line with our expectations, although this is by a considerable 0.070 Å. Progressing to the CCSD level, we see that UHF and ROHF bonds are essentially the same. We see that in going to the CCSD level, the ROHF bond is contracted only 0.025 Å from MBPT(2), so the MBPT(2) result is actually quite reasonable. The UHF bond lengthens 0.045 Å and show that it does not provide

Table 4.23. Electron affinity (kJ/mol) of CN at different levels of MBPT using UHF and ROHF references with the PVDZ basis.

	Electron Affinity[a]		Multiplicity	
	ROHF	UHF	UHF (No T_1)	UHF (With T_1)
SCF	271	223	2.406	—
MBPT(2)	284	374	2.368	—
MBPT(3)	300	353	2.354	2.291
SDQ-MBPT(4)	284	339	2.339	2.233
MBPT(4)	278	350	2.336	2.236
CCSD	276	276	—	2.043

[a]Experimental value is 367 ± 3 kJ/mol.

a good description at MBPT(2). This result parallels very well with the value of the multiplicity, also shown in Table 4.22. The UHF-SCF wavefunction is highly spin contaminated with a multiplicity of 2.337. It is significantly improved at MBPT(2), being 2.233, but is still very contaminated. At the CCSD level, it is almost a pure spin state.

We determined the EA of CN with both UHF and ROHF references. Table 4.23 shows the EA for CN at different levels of MBPT calculated using the CCSD geometries, together with the UHF multiplicities. At the SCF level, we see that ROHF is closer than UHF to the experimental value of 367 kJ/mol, but is still almost 100 kJ/mol too small. At the correlated level, UHF appears to do a better job while ROHF is significantly below the experimental value. However, as SDQ-MBPT(4) is the fourth-order approximation to the infinite-order CCSD result, the UHF-MBPT electron affinity must converge to 276 kJ/mol, showing the low-order UHF-MBPT results to be fortuitous. Furthermore, it should be pointed out that UHF does a poor job of describing the geometry at MBPT(2). This would seem to indicate that at the MBPT(2) level, there is insufficient orbital relaxation to make up for the deficiencies in the UHF wavefunction. A measure of this is given by the multiplicity. Indeed, if we examine the multiplicity at each level of MBPT, also given in Table 4.23, we

Table 4.24. Electron affinity (kJ/mol) of CN at different levels of MBPT using UHF and ROHF references with the PVTZ basis.

	Electron Affinity[a]		Multiplicity	
	ROHF	UHF	UHF (No T_1)	UHF (With T_1)
SCF	305	262	2.341	—
MBPT(2)	356	432	2.307	—
MBPT(3)	366	409	2.295	2.237
SDQ-MBPT(4)	352	396	2.282	2.186
MBPT(4)	351	411	2.280	2.189
CCSD	344	344	—	2.041

[a]Experimental value is 367 ± 3 kJ/mol.

see that the wavefunction is still severely contaminated. We must conclude that the excellent agreement for UHF is merely a fortunate occurrence rather than the result of a fundamentally better description.

Turning our attention to the PVTZ results, we see the same trends in the geometry for UHF and ROHF in going from SCF to MBPT(2), and then to CCSD. ROHF behaves in the manner expected as the level of theory is increased, while UHF does not. With the PVTZ basis, the ROHF based MBPT electron affinities do a much better job than UHF, as seen in Table 4.24. We see that the variation of the ROHF EA's with level of theory is much less than that for UHF. The ROHF EA has a spread of only 15 kJ/mol while UHF has a spread of 36 kJ/mol. In addition, the ROHF results consistently remain below the experimental value while UHF overestimates considerably.

Since the use of augmented basis sets greatly improves the EA results for the first row atoms, we use the augmented PVDZ and PVTZ basis sets for CN. The optimized geometries and UHF multiplicities are given in Table 4.25. Not too surprisingly, we see very little change in the geometries between the augmented and unaugmented basis sets. This make sense since the additional p function is diffuse and would not be expected to play a significant role in molecular bonding. A more dramatic change

Table 4.25. Optimized geometries[a] for CN and CN^- using the PVDZ+ and PVTZ+ basis sets and UHF multiplicities.

	PVDZ+			PVTZ+		
	SCF	MBPT(2)	CCSD	SCF	MBPT(2)	CCSD
CN^- (RHF)	1.167	1.208	1.196	1.153	1.185	1.173
CN (UHF)	1.163	1.138	1.184	1.150	1.124	1.163
CN (ROHF)	1.139	1.210	1.184	1.129	1.186	1.164
UHF multiplicity	2.334	2.232	2.043	2.302	2.201	2.041

[a]Bond lengths are in Å.

Table 4.26. Electron affinity (kJ/mol) of CN at different levels of MBPT using UHF and ROHF references with the PVDZ+ basis.

	Electron Affinity[a]		Multiplicity	
	ROHF	UHF	UHF (No T_1)	UHF (With T_1)
SCF	299	250	2.404	—
MBPT(2)	316	406	2.366	—
MBPT(3)	331	382	2.353	2.289
SDQ-MBPT(4)	315	369	2.338	2.232
MBPT(4)	311	382	2.336	2.235
CCSD	307	307	—	2.043

[a]Experimental value is 367 ± 3 kJ/mol.

is seen for the EA's, shown along with the UHF multiplicities in Tables 4.26 and 4.27. The additional p function with the PVDZ basis adds approximately 30 kJ/mol to the predicted EA's at each level of theory for both UHF and ROHF. This leads the UHF PVDZ+ results to overestimate the EA while the ROHF PVDZ+ results are still below the experimental value. The spread in the EA values for UHF and ROHF are 37 and 20 kJ/mol, respectively. With the PVTZ+ basis, UHF significantly overestimates the EA while ROHF is essentially correct. The spread in EA's are now 38 and 13 kJ/mol for UHF and ROHF, respectively. The continued poor performance for UHF is again mirrored by the spin contamination using the augmented basis sets, with the multiplicities basically unchanged from those obtained with the unaugmented basis sets. Summarizing, ROHF-MBPT provides a better description of the CN

Table 4.27. Electron affinity (kJ/mol) of CN at different levels of MBPT using UHF and ROHF references with the PVTZ+ basis.

	Electron Affinity[a]		Multiplicity	
	ROHF	UHF	UHF (No T_1)	UHF (With T_1)
SCF	314	272	2.341	—
MBPT(2)	367	443	2.307	—
MBPT(3)	375	419	2.295	2.237
SDQ-MBPT(4)	362	405	2.282	2.186
MBPT(4)	362	422	2.280	2.189
CCSD	354	355	—	2.041

[a]Experimental value is 367 ± 3 kJ/mol.

system. This is based on its better accuracy upon improvement of the basis and in its consistency at each level of MBPT. The spread in EA values is much less than for UHF and is diminished by improving the basis, while the UHF spread remains about the same.

While this study of the CN system gives us good information for comparing ROHF and UHF based MBPT, we also wish to compare ROHF-MBPT to other methods which address the spin contamination problem. Handy, et. al. [20] have studied the cyano radical using their spin projection methods. In order to provide a direct comparison, we perform optimizations of CN using the same basis set as Handy, et. al. [20] at the MBPT(2) and CCSD levels of theory. The results are shown in Table 4.28, together with the projected results of Handy, et. al. At MBPT(2), the ROHF result is quite close to the experimental bond length of 1.172 Å, while the UHF result gives a much shorter bond length. The PUMP2(1) and PUMP2(2) methods, with elimination of the first and second contaminants, respectively, improve the UHF result, but not in a straightforward manner, as the elimination of two contaminants *gives a poorer bond length.* The electron affinities for CN at different levels of theory are shown in Table 4.29. As can be seen, the ROHF-MBPT(2) result is in very good agreement with the experimental value of 367 kJ/mol, while the UHF result is

Table 4.28. Optimized geometries (in Å) for CN[a] and CN^- using a $5s4p2d$ basis set[b].

	MBPT(2)	CCSD
CN^- (RHF)	1.186	1.174
CN (UHF)	1.124	1.165
CN (ROHF)	1.188	1.165
CN / PUMP2(1)[b]	1.164	—
CN / PUMP2(2)[b]	1.154	—

[a]The experimental value for R_e for CN is 1.172 Å.
[b]Reference [20]

Table 4.29. Electron affinities (kJ/mol) and selected multiplicities, 2S+1 values of CN at CCSD optimized geometries using a $5s4p2d$ basis set[a].

	Electron Affinity[b]		Multiplicity	
	ROHF	UHF	UHF (No T_1)	UHF (With T_1)
SCF	312	267	2.357	—
MBPT(2)	356	434	2.321	—
MBPT(3)	365	410	2.309	2.250
SDQ-MBPT(4)	352	397	2.296	2.198
MBPT(4)	350	413	2.293	2.201
CCSD	343	344	—	2.043

[a]Reference [20]
[b]Experimental value for the CN electron affinity is 367 ± 3 kJ/mol.

not. As the level of theory increases, the UHF results undergo large changes while the ROHF results do not. However, both references converge to the same result at CCSD, which attests to the powerful treatment of orbital relaxation in CC methods [44]. Additionally, the improvement in the spin multiplicity for the UHF wavefunction is slow as the level of perturbation theory is increased. Even with the infinite order CCSD method, the spin contamination is not completely eliminated. The PUMP2(1) and PUMP2(2) results are 358.4 and 364.9 kJ/mol, respectively, also in excellent agreement, but several points should be made about these methods.

Examining the geometries in Table 4.28, the PUMP2(1) result is essentially the same as the CCSD result, but it does not reflect the expected behavior for the MBPT(2) method. It is well known that MBPT(2) tends to overestimate the effect of correlation on bond lengths [43], so the MBPT(2) bond length should be longer than the full CI value. This also holds for the PUMP2(2) result, which falls back towards the UHF result. Additionally, the PUMP2(1) energy is lower than the PUMP2(2) energy (-92.5733 vs. -92.5708 hartrees). This is somewhat surprising for the following reason. Since we are studying the ground state of CN, we expect the contaminating quartet, sextet, ..., to lie higher in energy. The degree to which these higher multiplicity states mix into the ground state wavefunction is indicated by the average multiplicity and how far it is from the exact value. Since the ground state doublet is contaminated by higher energy multiplets, we expect the ground state energy to decrease with the removal of each successive contaminant, i.e., we are moving towards a wavefunction which reflects the pure doublet spin state. Since removal of the second contaminant in CN raised the energy, one must wonder what affect the projection operator is having on the wavefunction. An additional indication of aberrant behavior is found in the average multiplicity. PUMP2(1) gives a value of 1.941, while PUMP2(2) gives the correct value of 2.000.

The reasons for this behavior have been explained in a recent paper by Koga, et. al. [45]. They examined the effect of using approximate spin projection equations versus the exact projection equations for elimination of spin contamination in the UHF wavefunction. In the limit of including all possible higher multiplets, the approximate equations give the same result as the exact equations. By examining the leading terms in the error for $\langle \hat{S}^2 \rangle$ and $\langle \hat{H} \rangle$ after elimination of the first and second contaminants, they saw that the approximate projection changes the sign of the lead error upon each projection. This means that for only one projection, the leading term in the error for the approximate scheme is negative, while it remains positive for the exact expression. After two projections, the sign for the lead term in the approximate expression is again positive, in agreement with the exact formula. Depending on the magnitude of the contamination, and the importance of the first contaminant, it is possible to get a value of $\langle \hat{S}^2 \rangle$ which is below the exact value. A similar situation holds for the energy.

Extending this examination to the PUMP2 projection schemes, Koga, et. al. [45] demonstrated that the behavior seen for UHF projection also holds for the PUMP2 schemes. The PUMP2(1) projection results in a lead error term which is negative for the energy, while PUMP2(2) has a positive lead error in the energy. They also point out that similar behavior is present for the value of $\langle \hat{S}^2 \rangle$. Their conclusion is that the approximate spin projection equations should not be used for single projection, but should always be used with double projection. The work of Koga, et. al. provides a theoretical confirmation of the observation that PUMP2(1) gives errant results. However, it will be shown later for Li_3 that this particular drawback is not always important.

Given this discussion of how the wavefunction can be significantly modified, it raises the issue of the validity of using the projected energies in conjunction with closed-shell RHF results. Ostensibly, any RHF-MBPT result is unprojected since it

is not contaminated. Similarly, the ROHF-MBPT results are unprojected ones and it is logical to conclude that properties determined as differences between RHF and ROHF-MBPT are more theoretically satisfying. Also, PUMP methods are no longer rigorously size-extensive. This deficiency keeps them from being suitable methods for extended systems, violating the rationale for all many-body methods. Another factor which limits the usefulness of the PUMP2(2) method, however, is the expense required to routinely perform calculations at this level. Handy, et. al. [20] point out the substantial task of putting together a practical evaluation of PUMP2(2) derivatives, which is critical for wide acceptance of any method. They reported needing some 8000 lines of FORTRAN to implement the gradients. They also report that the cost of performing a PUMP2(2) energy and gradient calculation is typically three times that required for a UHF-MBPT(2) energy and gradient. This expense highlights the economy of the ROHF-MBPT approach, which requires essentially the same amount of time as a UHF-MBPT(2) energy and gradient. Therefore, for systems which are spin-contaminated and for which a reliable ROHF reference can be obtained, this is the more efficient method for introducing electron correlation.

4.4 The Li_3 Molecule

Handy, et. al. [20] also considered this molecule as it contains a significant amount of spin contamination. Our first comparison, therefore, is to their results. We optimize the structure of Li_3 using the 6-31G* basis at the SCF, MBPT(2), and CCSD levels of theory with both UHF and ROHF references. The geometries, energies, and average multiplicity are given in Table 4.30. As can be seen, Li_3 is very heavily spin contaminated, although it is essentially eliminated at the CCSD level. As with CN, we have also calculated the MBPT energies for both UHF and ROHF using the CCSD optimized geometries. These energies, as well as the binding energy per Li atom, are

Table 4.30. UHF and ROHF geometries[a] of C_{2v} Li_3 at several levels of theory using the 6-31G* basis set.

	SCF	MBPT(2)	CCSD
UHF			
R(Li-Li)	2.867	2.820	2.820
θ	70.51	75.38	72.74
Energy	-22.313306	-22.330439	-22.347708
Multiplicity	2.421	2.376	2.028
ROHF			
R(Li-Li)	2.900	2.856	2.820
θ	76.12	74.30	73.00
Energy	-22.301898	-22.333167	-22.347056
Multiplicity	2.000	2.000	2.000

[a]Bond lengths in Å; bond angles in degrees.

given in Table 4.31. There are two experimental values for the binding energy: 13.8 ± 1.3 kcal/mol [46] and 12.10 ± 0.24 kcal/mol [47]. At the MBPT(2) level, we see the ROHF value (7.84 kcal/mol) is between the UHF value (7.26 kcal/mol) and the PUMP2 value (8.60 kcal/mol). While this seems to validate PUMP2, one must remember the costs associated with PUMP2. As alluded to earlier, the PUMP2(1) result for the the average multiplicity is not poor; rather, it gives a value of 2.000. The effect on the energy in going to PUMP2(2) is also not as dramatic as with CN, with the PUMP2(2) energy only 0.001 millihartree higher in energy. However, this general approach has not been applied to higher levels of perturbation theory. We see from Table 4.31 that the ROHF binding energy is consistently better than the UHF value, except at the CCSD level, where the powerful corrective ability causes the reversal of the UHF/ROHF ordering.

Another interesting facet to Li_3 lies in determining its structure and vibrational frequencies. This molecule, as well as the other triatomic alkali metal molecules, are known to be pseudo-rotators. The structure presented is for one of the two possible C_{2v} structures which result from Jahn-Teller distortion from D_{3h}. To further characterize this geometry, the harmonic vibrational frequencies are determined via

Table 4.31. Total energies for C_{2v} Li_3 and binding energies (BE) per Li atom using the CCSD optimized geometry.

	UHF		ROHF	
	Energy[a]	BE[b]	Energy[a]	BE[b]
SCF	-22.313212	3.99	-22.301450	1.54
MBPT(2)	-22.330365	7.28	-22.333067	7.84
MBPT(3)	-22.335964	8.44	-22.342155	9.74
SDQ-MBPT(4)	-22.338934	9.06	-22.345308	10.39
MBPT(4)	-22.339168	9.10	-22.346065	10.55
CCSD	-22.347708	10.89	-22.347056	10.75

[a]Total energies in hartrees.
[b]Binding energies in kcal/mol.

Table 4.32. Harmonic frequencies (intensities)[a] for C_{2v} Li_3 at several levels of theory using the 6-31G* basis set.

	SCF	MBPT(2)	CCSD	Fitted[b]
UHF				
a_1	165 (16.9)	150 (1.5)	169 (11.0)	130
b_2	240 (4.1)	221 (22.4)	193 (14.5)	190
a_1	315 (17.3)	332 (8.6)	325 (23.6)	349
ROHF				
a_1	136 (7.7)	155 (10.1)	166 (12.1)	130
b_2	209 (40.4)	282 (820.1)	190 (31.2)	190
a_1	308 (14.4)	316 (18.7)	323 (24.1)	349

[a]Frequencies in cm^{-1}; intensities in km/mol.
[b]Reference [48].

a finite difference of analytic gradients and are shown in Table 4.32. Also included are the frequencies determined by Thompson, et al. [48] via analytic fits of the Li_3 potential energy surface. We see that the SCF results for ROHF are actually very reasonable, but this is just a fortuitous circumstance. The UHF SCF results are, as expected, somewhat off the mark with respect to the fitted values. If we look at MBPT(2), we see that ROHF is performing markedly worse than UHF, and, based on some of the previous results, is somewhat disturbing. The b_2 frequency deviates substantially from the fitted value and has an intensity which is very large. As it

turns out, this is due to the fact that the ROHF reference function *breaks symmetry*, a situation to which ROHF is more susceptible than UHF. The results given so far are for the symmetric solution. If the C_{2v} molecular symmetry is imposed on the wavefunction, then one can obtain the symmetric solution. However, if the calculation is allowed to proceed in C_1 symmetry, the additional freedom allows the wavefunction to optimize into a lower symmetry than the molecular framework. Therefore, the large discrepancy in the MBPT(2) frequencies could be attributed to this particular shortcoming of the ROHF reference. A further indication of the corrective power of CCSD is to examine the CCSD frequencies. At this level, the ROHF and UHF results are essentially indistinguishable. In addition, they are very close to the fitted values.

4.5 The FCS radical

This molecule is of particular interest since an experimental emission [49] attributed to the fluorothioformyl radical FCS has been withdrawn [50]. The withdrawal was made because the original experiment was repeated with isotopic substitution and the spectra remained unchanged, indicating an emitter other than FCS. With this in mind, Chan and Goddard [51] conducted a study into the characterization of this radical and the chloro analog, ClCS. They pointed out in this work that due to severe spin contamination of the UHF reference, MBPT(2) work using this reference was suspect. They utilized an ROHF reference to conduct their most accurate calculations, but used configuration interaction with singles and doubles (CISD) to add the electron correlation. For these reasons, the FCS molecule provides an excellent opportunity for comparison of two different single reference methods (CI and MBPT) using the ROHF reference.

We used two different basis sets in studying FCS. The first was the 6-31G* basis, since this was used by Chan and Goddard. The second was a better, full DZP

Table 4.33. UHF and ROHF optimized geometries[a] for the $^2A'$ state of FCS using two different basis sets at several levels of theory.

	UHF			ROHF			
	SCF	MBPT(2)	CCSD	SCF	MBPT(2)	CCSD	RCISD[b]
6-31G*							
R(F-C)	1.288	1.301	1.318	1.280	1.322	1.318	1.305
R(C-S)	1.584	1.543	1.583	1.572	1.576	1.583	1.572
θ(FCS)	131.27	133.91	130.94	132.17	131.43	130.88	131.8
DZP							
R(F-C)	1.287	1.300	1.317	1.280	1.322	1.317	—
R(C-S)	1.576	1.532	1.572	1.563	1.565	1.573	—
θ(FCS)	131.33	133.94	131.02	132.27	131.49	130.96	—

[a]Bond lengths in Å; bond angles in degrees.
[b]Reference [51].

quality basis. The DZP basis for C and F consists of the standard Dunning (9*s*,5*p*) primitive set [52] contracted to [4*s*,2*p*] and augmented with a single polarization function [53]. The DZP basis for S started from the (12*s*,9*p*) primitive set of McLean and Chandler [54] contracted to [6*s*,4*p*], and augmented with a single *d* function [55]. The geometries obtained with the UHF and ROHF references at several levels of theory are shown in Table 4.33. In addition, we also show the RCISD (ROHF-CISD) results from Chan and Goddard. The UHF results at the SCF and MBPT(2) level, as well as the ROHF SCF results, using the 6-31G* basis are the same as Chan and Goddard. Since there are no experimental values for the geometry, we shall use the CCSD results for the ROHF reference as our best estimate. We choose this over the RCISD results because CCSD is a size extensive method while CISD is not. As noted by Chan and Goddard, the bond angle is fairly invariant to level of theory, ranging from 130.8° to 133.9° in either basis set. With respect to the bond lengths, the F-C bond length increases with introduction of correlation and makes a similar increase in going from MBPT(2) to CCSD. The most notable change is the effect of correlation on the C-S bond length. The UHF SCF result is spuriously close to the

Table 4.34. Harmonic frequencies (intensities)[a] of FCS given at several levels of theory.

		UHF		RCISD[b]
	SCF	MBPT(2)	CCSD	
6-31G*				
a'	495 (3.8)	506 (0.1)	471 (0.7)	486
a'	941 (59.0)	1164 (26.9)	978 (26.0)	1013
a'	1466 (426.5)	1491 (1284.7)	1379 (418.2)	1429
DZP				
a'	497 (4.6)	510 (0.2)	474 (0.9)	—
a'	936 (74.4)	1145 (66.4)	970 (47.1)	—
a'	1460 (528.8)	1499 (1363.7)	1368 (464.2)	—
		ROHF		
6-31G*				
a'	505 (3.3)	476 (0.6)	470 (0.6)	—
a'	1050 (17.0)	976 (44.2)	973 (28.9)	—
a'	1480 (634.8)	1391 (369.0)	1376 (408.0)	—
DZP				
a'	508 (4.6)	480 (1.1)	473 (0.9)	—
a'	1049 (25.5)	963 (74.5)	966 (46.7)	—
a'	1477 (719.8)	1377 (412.1)	1364 (453.5)	—

[a]Frequencies are in cm^{-1}; intensities in km/mol.
[b]Reference [51].

CCSD result, but at the MBPT(2) level it is significantly shorter. This is in contrast to the ROHF-MBPT(2) result, which is only slightly shorter than the CCSD result. At the CCSD level, we see that using the UHF or ROHF reference essentially makes no difference. The bond angles are different by less than 0.1° with either basis. We can also see how the geometries compare at different levels of theory by examining the harmonic frequencies, which are given in Table 4.34. For the 6-31G* basis, we see that the ROHF-MBPT(2) results have outstanding agreement with the CCSD results. The RCISD results are reasonable, but are still not very close. One must also note that this example continues to demonstrate the powerful corrective abilities of CCSD, as the UHF and ROHF results are essentially the same.

We also wished to assess the effects of triple excitations on the geometry of FCS. The geometry was optimized at the CCSD(T) level using the DZP basis and the UHF reference. The F-C bond is 1.322 Å, the C-S bond is 1.577 Å, and the bond angle is 130.82°. These results indicate that triple excitations are not important in characterizing the potential surface. Therefore, we would suggest that the DZP CCSD results, be used as a guide for experiment in determining if FCS has been synthesized.

4.6 The N_2H molecule and N_2 + H transition state

The characterization of the reaction N_2 + H has been of interest recently because of its postulated importance in combustion reactions. Several theoretical and experimental studies have been conducted to further understand this molecule [56, 57, 58, 59]. The most extensive set of calculations published to date are those of Walch, Duchovic, and Rohlfing (WDR) [58] and a subsequent study by Walch [59]. They used a reasonably large ANO basis set and performed CASSCF/CCI calculations. The later study by Walch further characterized the potential surface, but essentially did not change the results of the earlier paper. For purposes of evaluating our methods, we shall use the results of WDR as the currently best available in the literature.

Optimizations of the N_2H minimum and N_2 + H transition state were performed at the SCF, MBPT(2), and CCSD levels of theory using the PVDZ basis. These geometries, together with the energies and average multiplicities, are reported in Tables 4.35 and 4.36 for the PVDZ basis. The geometries of WDR are also given. For the N_2H minimum at MBPT(2), we see that once again, the UHF structure is significantly different than that for ROHF. The behavior for the N-N bond is incorrect, resulting in a contraction of the bond while ROHF gives the expected bond lengthening. The N-N bond contraction for UHF also is probably responsible for the large increase ($\approx 8°$) in the NNH angle. At the CCSD level, both UHF and ROHF

Table 4.35. UHF and ROHF optimized geometries[a] for the $^2A'$ state of N_2H using the PVDZ basis set at several levels of theory.

	SCF	MBPT(2)	CCSD	WDR[b]
UHF				
R(N-N)	1.178	1.150	1.190	1.197
R(N-H)	1.036	1.061	1.060	1.062
θ(NNH)	112.39	120.05	114.87	116.3
Energy	-109.439315	-109.737808	-109.762186	
Multiplicity	2.124	2.055	2.014	
ROHF				
R(N-N)	1.167	1.185	1.190	
R(N-H)	1.030	1.058	1.060	
θ(NNH)	112.98	117.82	114.95	
Energy	-109.431025	-109.746816	-109.761990	
Multiplicity	2.000	2.000	2.000	

[a]Bond lengths in Å; bond angles in degrees.
[b]Reference [58].

Table 4.36. UHF and ROHF optimized geometries[a] for the transition state of the N_2 + H reaction using the PVDZ basis set at several levels of theory.

	SCF	MBPT(2)	CCSD	WDR[b]
UHF				
R(N-N)	1.117	1.115	1.137	1.136
R(N-H)	1.394	1.347	1.417	1.457
θ(NNH)	113.16	122.54	117.02	118.6
Energy	-109.418204	-109.724881	-109.746636	
Multiplicity	2.133	2.092	2.013	
ROHF				
R(N-N)	1.105	1.152	1.136	
R(N-H)	1.336	1.427	1.413	
θ(NNH)	116.93	117.83	117.30	
Energy	-109.401681	-109.743730	-109.745685	
Multiplicity	2.000	2.000	2.000	

[a]Bond lengths in Å; bond angles in degrees.
[b]Reference [58].

give essentially the same structure. This is very close to the results of WDR, with the N-N bond being 0.007 Å shorter and the angle 1.4° smaller. Comparing the MBPT(2) and CCSD geometries, we observe that ROHF gives a much better qualitative result than UHF.

The geometry of the transition state further emphasizes the shortcomings of the UHF reference. Once again, we see a slight contraction of the N-N bond length in going from SCF to MBPT(2), which is corrected at the CCSD level. The ROHF reference has the anticipated N-N behavior at MBPT(2), the bond increasing in length $\approx$ 0.05 Å. The CCSD results for ROHF and UHF are essentially the same, although the N-H bond for ROHF is slightly (0.004 Å) shorter than the UHF result. Comparing the CCSD results to the work of WDR, we see the largest difference in the N-H bond length; this is most likely due to the larger basis set used by WDR. Their basis set gives more flexibility in this region whereas the PVDZ basis is deficient. If we look at the MBPT(2) results, we see that ROHF gives remarkably good agreement with the CCSD results, with the N-H bond at 1.427 Å versus 1.347 Å for UHF. The behavior of the N-H bond in going from MBPT(2) to CCSD with the ROHF reference is also as expected; the bond contracts slightly. The geometries given here indicate that ROHF is doing a very good job in determining the primary qualities of the molecule at only the MBPT(2) level of theory.

The harmonic frequencies and intensities of the minima and transition states are shown in Table 4.37 for the PVDZ basis. We see that the ROHF-MBPT(2) frequencies are very close to the CCSD results, in stark contrast to the UHF-MBPT(2) frequencies. The N-N stretch (2817 cm^{-1}) is $\approx$ 1000 cm^{-1} too large, while the ROHF N-N stretch is only 17 cm^{-1} too large. Another important point is to note the inappropriate value of the UHF-MBPT(2) frequency for the N-N stretch. The optimized MBPT(2) geometry for N_2 with the PVDZ basis is 1.129 Å and has a frequency of 2179 cm^{-1}. First, the N-N bond in N_2H is longer than in N_2 at the MBPT(2) level,

Table 4.37. Harmonic frequencies (intensities)[a] for UHF and ROHF minima and transition states for N_2H using the PVDZ basis set.

	SCF	MBPT(2)	CCSD	WDR[b]
UHF				
Minimum				
a'	1238 (107.9)	1028 (154.3)	1118 (98.1)	1070
a'	1661 (7.3)	2817 (68.6)	1858 (18.2)	1583
a'	3237 (5.6)	2962 (103.2)	2891 (61.1)	2744
Transition State				
a'	1880i (976.7)	2246i (2568.5)	1647i (916.0)	1662i
a'	886 (10.5)	800 (16.6)	770 (4.6)	771
a'	2146 (46.6)	2889 (223.3)	2153 (55.7)	2072
ROHF				
Minimum				
a'	1237 (120.4)	1001 (157.7)	1121 (97.1)	
a'	2051 (22.9)	1869 (26.2)	1852 (17.1)	
a'	3394 (0.5)	2923 (25.6)	2893 (60.9)	
Transition State				
a'	3540i (6912.2)	1880i (1233.6)	1793i (1121.7)	
a'	877 (14.6)	771 (2.3)	772 (5.0)	
a'	2420 (108.0)	1986 (31.1)	2159 (58.7)	

[a]Frequencies are in cm^{-1}; intensities in km/mol.
[b]Reference [58].

but the frequency is ≈ 640 cm^{-1} too large. Curtiss, et. al. [56] noted similar behavior at the UHF-MBPT(3) level (the N-N stretch in N_2H being 85 cm^{-1} larger than in free N_2), but attributed it to a poor basis set (6-31G**).

In order to test this hypothesis, we optimized N_2H and N_2 at the MBPT(3) level using UHF and RHF references, respectively. The N_2H geometry is R(N-N)=1.155 Å, R(N-H)=1.055 Å, and θ(NNH)=117.14°. The resulting frequencies and intensities are 1074 cm^{-1} (135.2 km/mol), 2627 cm^{-1} (79.3 km/mol), and 2996 cm^{-1} (39.8 km/mol). The MBPT(3) N_2 stretching frequency is 2534 cm^{-1}. We observe essentially the same behavior with the PVDZ basis as that observed by Curtiss, et. al. [56] The N-N strech in N_2H is 93 cm^{-1} larger than in free N_2, despite having a longer bond length. The results from this work seem to indicate that this phenomenon is not merely a basis set problem, since the PVDZ basis was designed for use in correlated calculations. Instead, it appears to be a breakdown of UHF-MBPT. This poor performance has been attributed to the poor description which single reference methods provide in multiply-bonded systems [60, 61], and was explicitly pointed out by WDR as a necessity for using a multireference approach. With this in mind, it would appear difficult to reconcile the quite excellent agreement between ROHF-MBPT(2) and CCSD. The ROHF-MBPT(2) N-N stretch is 310 cm^{-1} smaller than in free N_2 and is what one would expect, given the longer N-N bond in N_2H.

One point to note, however, is that the UHF reference function is moderately spin contaminated (average multiplicity = 2.078), and this could very well account for its erratic performance at MBPT(2) and MBPT(3). Therefore, rather than being a deficiency in single reference methods, it may only be a poor starting point in this case. A more conclusive comparison between UHF and ROHF at finite order must be deferred until the implementation of fourth-order gradients for ROHF.

The transition state frequencies show a similar trend, with the ROHF-MBPT(2) results very close to CCSD and the UHF results not. The UHF-CCSD results for

Table 4.38. Relative energy of N_2H with respect to N_2 + H and height of dissociation barrier with respect to N_2H at PVDZ optimum geometries (kcal/mol).

	SCF		MBPT(2)		CCSD	
	ΔE	Barrier	ΔE	Barrier	ΔE	Barrier
UHF	10.09	13.25	22.50	8.11	7.30	9.76
ROHF	15.30	18.41	16.85	1.94	7.42	10.23

WDR results: $\Delta E = 3.01$, barrier = 12.15.

the transition state are close to those of WDR; the same is true for ROHF except for the reaction coordinate mode (N$\cdots$H). The ROHF result indicates a stronger motion through the transition state than UHF or the WDR work. In order to understand this point better, we need to examine the predicted barrier heights.

The relative energies of N_2H with respect to N_2 + H and the barrier heights for the optimized geometries at the SCF, MBPT(2), and CCSD levels are shown in Table 4.38. Looking at the barrier height at these levels, we see a correspondence between the barrier height and the magnitude of the imaginary frequency for UHF and ROHF. The ROHF barrier is larger at the SCF and CCSD levels, and so is the imaginary frequency. At MBPT(2), the UHF barrier is larger and the same follows for the imaginary frequency. Comparing to the results of WDR shows that at the best level (CCSD), the barrier is underestimated. With this quality of basis set, we are at a level where the geometry is less likely to be susceptible to large changes as a function of increasing basis set quality (except for the N-H transition state bond as stated earlier). It is possible, then, that with a better basis set the CCSD differences between UHF and ROHF for the imaginary mode may grow smaller, in addition to reaching better agreement with WDR.

To further evaluate the performance of ROHF-MBPT, we calculate the MBPT energies of the minima and transition states for UHF and ROHF using the CCSD geometries. These energies, together with the UHF multiplicities, are shown in Tables 4.39 and 4.40 for the PVDZ basis and in Tables 4.46 and 4.47. As with all

Table 4.39. MBPT energies using UHF and ROHF references for the $^2A'$ state of N_2H using the PVDZ basis at the CCSD optimized geometry.

	UHF	(Mult.) No T_1	(Mult.) With T_1	ROHF
SCF	-109.438402	2.155	a	-109.428938
MBPT(2)	-109.732363	2.135	a	-109.746667
MBPT(3)	-109.744844	2.130	2.101	-109.752964
SDQ-MBPT(4)	-109.754103	2.125	2.077	-109.761317
MBPT(4)	-109.764649	2.125	2.077	-109.774277

[a]There is no T_1 contribution at the SCF and MBPT(2) levels of theory.

Table 4.40. MBPT energies using UHF and ROHF references for the transition state of N_2H using the PVDZ basis at the CCSD optimized geometry.

	UHF	(Mult.) No T_1	(Mult.) With T_1	ROHF
SCF	-109.416664	2.172	a	-109.399333
MBPT(2)	-109.722128	2.145	a	-109.743143
MBPT(3)	-109.727494	2.136	2.100	-109.735337
SDQ-MBPT(4)	-109.739354	2.128	2.071	-109.746397
MBPT(4)	-109.752187	2.127	2.072	-109.763122

[a]There is no T_1 contribution at the SCF and MBPT(2) levels of theory.

the previous work at the MBPT level, we show the change in the multiplicity both with and without T_1. We see that MBPT improves the multiplicity, especially with inclusion of T_1, but that even at MBPT(4), the wavefunction still remains contaminated. The relative energies and barrier heights at the different MBPT levels with the CCSD geometries are shown in Table 4.41. We see that at the various levels of MBPT, the barrier height is consistently underestimated with respect to the WDR work. Following the argument about basis set size, we would expect the energies to

Table 4.41. Relative energy of N_2H with respect to N_2 + H and height of dissociation barrier at several levels of theory using CCSD optimized geometries with the PVDZ basis set (kcal/mol).

	SCF	MBPT(2)	MBPT(3)	SDQ-MBPT(4)	MBPT(4)
ΔE					
UHF	8.23	25.50	13.16	13.43	16.36
ROHF	14.17	16.52	8.07	8.91	10.32
Barrier Height					
UHF	13.64	6.42	10.89	9.25	7.82
ROHF	18.58	2.21	11.06	9.36	7.00

WDR results: $\Delta E = 3.01$, barrier = 12.15.

be more sensitive to basis, and so the relative energies may be improved by using a larger basis set.

In order to explore this effect, we repeat all optimizations using the PVTZ basis set. The geometries of the N_2H minimum are shown in Table 4.42. As one would expect, the improved basis leads to a slight contraction of all the bond lengths, along with a concomitant increase in the bond angles. For the transition state geometries, shown in Table 4.43, the N-N bond contracts slightly while the N-H bond lengthens for both UHF and ROHF. The bond angles remain essentially unchanged. The behavior for the N_2H transition state using the PVDZ basis is seen again with the PVTZ basis. The ROHF-MBPT(2) transition state is in remarkably good agreement with that of WDR. At the CCSD level, however, both UHF and ROHF still have a shorter N-H bond than WDR.

The harmonic frequencies and intensities for the minimum and the transition state with the PVTZ basis are shown in Table 4.44. As with the geometries, there is no substantive change upon improvement of the basis. The UHF-MBPT(2) result for the N-N stretch at the N_2H minimum is still too large and not qualitatively correct.

Since the PVTZ basis is comparable to that used by WDR, we are still disturbed by the disagreement between the N-H bond lengths for the transition state. Feeling

Table 4.42. UHF and ROHF optimized geometries[a] for the $^2A'$ state of N_2H using the PVTZ basis set at several levels of theory.

	SCF	MBPT(2)	CCSD	WDR[b]
UHF				
R(N-N)	1.166	1.140	1.171	1.197
R(N-H)	1.028	1.045	1.044	1.062
θ(NNH)	112.51	121.03	116.30	116.3
Energy	-109.469525	-109.864110	-109.882387	
Multiplicity	2.096	2.042	2.011	
ROHF				
R(N-N)	1.158	1.167	1.171	
R(N-H)	1.022	1.046	1.044	
θ(NNH)	113.89	119.56	116.18	
Energy	-109.460967	-109.871597	-109.882200	
Multiplicity	2.000	2.000	2.000	

[a]Bond lengths in Å; bond angles in degrees.
[b]Reference [58].

Table 4.43. UHF and ROHF optimized geometries[a] for the transition state of the N_2 + H reaction using the PVTZ basis set at several levels of theory.

	SCF	MBPT(2)	CCSD	WDR[b]
UHF				
R(N-N)	1.105	1.102	1.116	1.136
R(N-H)	1.384	1.351	1.425	1.457
θ(NNH)	113.01	123.17	117.61	118.6
Energy	-109.448605	-109.848808	-109.864372	
Multiplicity	2.116	2.080	2.012	
ROHF				
R(N-N)	1.094	1.131	1.115	
R(N-H)	1.323	1.440	1.417	
θ(NNH)	117.73	117.90	117.91	
Energy	-109.432725	-109.864051	-109.863509	
Multiplicity	2.000	2.000	2.000	

[a]Bond lengths in Å; bond angles in degrees.
[b]Reference [58].

Table 4.44. Harmonic frequencies (intensities)[a] for UHF and ROHF minima and transition states for N_2H using the PVTZ basis set.

	SCF	MBPT(2)	CCSD	WDR[b]
UHF				
Minimum				
a'	1234 (114.9)	1053 (158.1)	1138 (106.4)	1070
a'	1707 (3.3)	2803 (65.5)	1899 (16.5)	1583
a'	3237 (5.5)	2972 (55.0)	2954 (42.4)	2744
Transition State				
a'	1899i (1069.9)	2228i (2656.6)	1615i (875.2)	1662i
a'	866 (9.9)	788 (14.1)	757 (4.1)	771
a'	2170 (56.0)	2757 (241.3)	2197 (73.2)	2072
ROHF				
Minimum				
a'	1238 (126.5)	1022 (161.5)	1141 (105.3)	
a'	2023 (21.9)	1896 (26.6)	1880 (15.2)	
a'	3393 (0.4)	2910 (26.4)	2960 (41.1)	
Transition State				
a'	3419i (6877.0)	2097i (1397.3)	1710i (1030.6)	
a'	881 (13.9)	742 (2.5)	763 (4.5)	
a'	2398 (118.6)	2011 (43.4)	2200 (75.9)	

[a]Frequencies are in cm^{-1}; intensities in km/mol.
[b]Reference [58].

Table 4.45. UHF-CCSD(T) optimized geometries[a] of the N_2H minimum and transition state using the PVDZ basis set.

	Minimum	Transition state
R(N-N)	1.193	1.141
R(N-H)	1.064	1.413
θ(NNH)	115.19	117.45

[a]Bond lengths in Å; bond angles in degrees.

that we are perhaps missing some important contribution due to higher excitations, we assess the effect of triple excitations on the geometry. We optimize the N_2H minimum and transition state at the CCSD(T) level using the UHF reference and PVDZ basis set. The geometries are shown in Table 4.45. At the N_2H minimum, the bond lengths became slightly longer than for CCSD. This brought the geometry into slightly better agreement with WDR. For the transition state, the N-N bond lengthened by 0.004 Å, but the N-H bond contracted by 0.004 Å. Since the difference between the transition state N-H bond lengths is the point we are attempting to address, we see that triples increase the disagreement. We would anticipate that if a CCSD(T) optimization were performed with the PVTZ basis, the N-H bond would lengthen slightly. However, it would still be significantly shorter than that of WDR. On the basis of the present calculations, it would appear that the CASSCF/CCI result is slightly overestimating the N-H transition state bond length, although different basis set choices can affect the answer. It is quite likely that if the geometry could be determined experimentally, the bond would be in the range 1.41-1.45 Å.

Turning our attention to the energetics, Tables 4.46 and 4.47 show the total MBPT energies and UHF multiplicities for the N_2H minimum and transition state for the ROHF and UHF references. From these energetics we can determine the relative energies and barrier heights as we did for the PVDZ basis. These results are shown in Tables 4.48 and 4.49. Looking first at the energies determined at the optimized

Table 4.46. MBPT energies using UHF and ROHF references for the $^2A'$ state of N_2H using the PVTZ basis at the CCSD optimized geometry.

	UHF	(Mult.) No T_1	(Mult.) With T_1	ROHF
SCF	-109.469034	2.155	a	-109.459961
MBPT(2)	-109.860577	2.090	a	-109.871365
MBPT(3)	-109.870736	2.097	2.065	-109.875980
SDQ-MBPT(4)	-109.877914	2.083	2.047	-109.882520
MBPT(4)	-109.895993	2.082	2.048	-109.903027

[a]There is no T_1 contribution at the SCF and MBPT(2) levels of theory.

Table 4.47. MBPT energies using UHF and ROHF references for the transition state of N_2H using the PVTZ basis at the CCSD optimized geometry.

	UHF	(Mult.) No T_1	(Mult.) With T_1	ROHF
SCF	-109.447964	2.132	a	-109.433380
MBPT(2)	-109.847745	2.109	a	-109.863454
MBPT(3)	-109.850561	2.102	2.073	-109.855367
SDQ-MBPT(4)	-109.860396	2.096	2.050	-109.864399
MBPT(4)	-109.881081	2.094	2.051	-109.889031

[a]There is no T_1 contribution at the SCF and MBPT(2) levels of theory.

Table 4.48. Relative energy of N_2H with respect to N_2 + H and height of dissociation barrier with respect to N_2H at PVTZ optimum geometries (kcal/mol).

	SCF		MBPT(2)		CCSD	
	ΔE	Barrier	ΔE	Barrier	ΔE	Barrier
UHF	11.00	13.13	17.21	9.60	4.50	11.30
ROHF	16.37	17.72	12.51	4.74	4.62	11.73

WDR results: ΔE = 3.01, barrier = 12.15.

Table 4.49. Relative energy of N_2H with respect to N_2 + H and height of dissociation barrier at several levels of theory using CCSD optimized geometries with the PVTZ basis set (kcal/mol).

	SCF	MBPT(2)	MBPT(3)	SDQ-MBPT(4)	MBPT(4)
ΔE					
UHF	9.95	19.01	8.31	8.69	11.49
ROHF	15.65	12.24	5.02	5.80	7.07
Barrier Height					
UHF	13.22	8.05	12.66	10.99	9.36
ROHF	16.68	4.96	12.93	11.37	8.78

WDR results: $\Delta E = 3.01$, barrier = 12.15.

geometries, we see that at the SCF level, the relative energy between the N_2H minimum and separated fragments has increased slightly upon improving the basis while the barrier to dissociation has increased slightly. At the correlated level, the reverse is true. The relative energy has decrased while the barrier has increased. However, the barrier height is still underestimated by both methods when compared to WDR. The relative energy between the minimum and separated fragments is very close at the CCSD optimized geometry, being only about 1.5 kcal/mol over the estimate by WDR, but the ROHF reference does a much better job of approaching this value at finite order, being consistently lower than the UHF result. The variation in the barrier height at finite order, as seen in Table 4.49 is somewhat of a mystery. There does not appear to be much of a pattern to decide which reference gives a better barrier height, since the two references alternate in which gives an answer closer to CCSD (and WDR). This does not appear to be a basis set effect, since the variation holds for both the PVDZ and PVTZ basis sets. However, based on the description of the geometries, one must give serious consideration to use of the ROHF reference at finite order.

This molecular system provides another example where ROHF would be the reference function of choice. The ROHF-MBPT(2) geometry is qualitatively correct, so

a large basis set study at this level could provide valuable information without the extra expense of a CCSD calculation.

CHAPTER 5
CONCLUSIONS

This work has presented the development of a treatment of electron correlation which utilizes a reference which is an eigenfuction of spin. The driving force for this development has been the need to be able to address the effects of electron correlation in high-spin open-shell systems where the standard UHF reference suffers from contamination from higher spin multiplicity states. The ROHF reference provides an excellent starting point which alleviates this particular drawback of the UHF reference.

The implementation of ROHF-MBPT has exploited the properties of the CCSD equations to yield a computationally efficient method. This implementation potentially allows for the exploration of either large molecules with small to modest bases, or small molecules with very large bases. The wavefunction has been demonstrated to contain desirable properties and is often not only qualitatively correct, but quantitatively correct at even the MBPT(2) level of theory. Furthermore, the development of analytical expressions for the gradient of the energy and implementation at the MBPT(2) and CCSD levels has greatly expanded the usefulness of this method.

The small set of molecular systems studied in this work have demonstrated that the ROHF MBPT method is an excellent tool which overcomes many shortcomings of UHF based methods. However, it also has shown that situations can arise in which the ROHF reference may suffer from symmetry breaking. Another problem is that the ROHF method tends to localize unpaired electrons, and this may lead to a

qualitatively incorrect starting point. Such occurrences can cripple the study of some problems with an ROHF reference. In such situations, other approaches to dealing with the problem of UHF spin contamination might be used, especially infinite-order CC methods that have the advantage of being relatively insensitive to the starting reference function. In particular, UHF-CC methods can still deal with situations in which use of an ROHF reference is inappropriate, such as complete cleavage of a bond to go from a closed-shell system to two open-shell systems.

Finally, the implementation of the ROHF-MBPT methods has been done in a formally, and practically, efficient approach. Wherever the ROHF reference can be used, the most economical path to obtaining answers at the MBPT level will probably be with ROHF-MBPT, since it is general, has appropriate orbital invariance properties, is size-extensive, and has gradient techniques which are up to several times faster than those envisioned for projected techniques.

APPENDIX A

ALGEBRAIC DEVELOPMENT OF ROHF-MBPT ENERGIES

A.1 General Derivation

To present a general derivation that embraces most cases, our starting point will be the CCSDT equations [7, 8]. These may be written in terms of the usual cluster operators $T_n = \sum t_{ij\ldots}^{ab\ldots}\{a^\dagger i b^\dagger j \ldots\}$ as

$$\langle_i^a|f_{ov} + f_D T_1 + WT_1 + WT_2 + f_{ov}T_2 + WT_3 + WT_1T_2 + WT_1^2/2$$
$$+f_{ov}T_1^2/2 + WT_1^3/3!|0\rangle_C = 0 \tag{A.1}$$

$$\langle_{ij}^{ab}|W + f_D T_2 + WT_2 + WT_1 + f_{ov}T_3 + WT_3 + WT_2^2/2$$
$$+WT_1T_2 + f_{ov}T_1T_2 + WT_1^2/2$$
$$+WT_1^2T_2/2 + WT_1T_3 + WT_1^3/3! + WT_1^4/4!|0\rangle_C = 0 \tag{A.2}$$

$$\langle_{ijk}^{abc}|f_D T_3 + WT_2|WT_3 + WT_2^2/2 + f_{ov}T_2^2/2 + WT_1T_2 + WT_2T_3 + WT_1T_3$$
$$+f_{ov}T_1T_3 + WT_1^2T_2/2 + WT_1T_2^2/2 + WT_1^2T_3/2 + WT_1^3T_2/3!|0\rangle_C = 0 \tag{A.3}$$

where $|0\rangle$ represents the reference function and $\langle_i^a|$, $\langle_{ij}^{ab}|$, and $\langle_{ijk}^{abc}|$ represent all single, double, and triple excitations, respectively, from the reference funciton. The energy is given by

$$E = \langle 0|H|0\rangle + \Delta E \tag{A.4}$$
$$\Delta E = \langle 0|WT_2 + WT_1^2/2 + f_{ov}T_1|0\rangle = E_2 + E_3 + E_4 + \cdots$$

The normal ordered Hamiltonian is

$$H_N = H - \langle 0|H|0\rangle = f + W = \sum_{pq} f_{pq}\{p^\dagger q\} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{p^\dagger q^\dagger sr\} \qquad (A.5)$$

Normal ordering has the advantage that the correlation correction, W, is entirely separated from the orbital relaxation part f.

In particular, the one-particle part of the Hamiltonian is

$$\begin{aligned} f &= \sum_i f_{ii}\{i^\dagger i\} + \sum_a f_{aa}\{a^\dagger a\} + \sum_{i<j} f_{ij}\{i^\dagger j\} + \sum_{a<b} f_{ab}\{a^\dagger b\} \\ &\quad + \sum_{ia} f_{ia}\left[\{i^\dagger a\} + \{a^\dagger i\}\right] \\ &= -D_n + f_{oo} + f_{vv} + f_{ov} = f_D + f_{ov} \end{aligned} \qquad (A.6)$$

where D_n indicates the diagonal elements of f, f_{oo} indicates the non-diagonal part of the occupied-occupied block, f_{vv} the non-diagonal virtual-virtual block, and f_{ov} the occupied-virtual block of the Fock matrix, i.e. $f_{pq} = \langle p|h|q\rangle + \sum_{j=1}^{occ}\langle pj||qj\rangle$. The C indicates that all products involve common W or f indices with the attached T operators (i.e. are "connected"). Making contractions of the second-quantized operators gives explicit orbital-based equations.

It is well known that iterating the CC equations defines various orders in perturbation theory. In the usual canonical SCF case, $f_{oo} = 0$, $f_{vv} = 0$, $f_{ov} = 0$ and $D_n = (\epsilon_i + \epsilon_j + \cdots - \epsilon_a - \epsilon_b - \cdots)$ so

$$\langle {}^a_i|D_1T_1|0\rangle = (\epsilon_i - \epsilon_a)\, t_i^a \qquad (A.7)$$

$$\langle {}^{ab}_{ij}|D_2T_2|0\rangle = (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)\, t_{ij}^{ab} \qquad (A.8)$$

Using the projection operators Q_n to indicate projection on the n-excitations, $P = |0\rangle\langle 0|$, with $E_n = \langle WT_2^{(n-1)}\rangle$ through fourth-order terms, we have

$$Q_2D_2T_2^{(1)}P = Q_2WP \qquad (A.9)$$

$$\Delta E = \langle WT_2^{(1)} \rangle = E_2 \tag{A.10}$$

$$Q_2 D_2 T_2^{(2)} P = WT_2^{(1)} P \tag{A.11}$$

$$\Delta E = \langle WT_2^{(2)} \rangle = E_2 + E_3 \tag{A.12}$$

$$Q_1 D_1 T_1^{(2)} P = Q_2 W T_2^{(1)} P \tag{A.13}$$

$$Q_2 D_2 T_2^{(3)} P = Q_2 \left(WT_2^{(2)} + WT_2^{(1)} T_2^{(1)} / 2 + WT_1^{(2)} + WT_3^{(2)} \right) P \tag{A.14}$$

$$Q_3 D_3 T_3^{(2)} P = Q_3 \left(WT_2^{(1)} \right) P \tag{A.15}$$

$$\Delta E = \langle WT_2^{(3)} \rangle = E_2 + E_3 + E_4^D + E_4^Q + E_4^S + E_4^T \tag{A.16}$$

and, of course, higher order terms can easily be generated in a similar way.

In the ROHF case, we take our orbitals from a high spin, single determinant ROHF calculation. However, in the spin orbital basis, $f_{ov} \neq 0$, so operationally we will treat the problem as a non-Hartree-Fock case. Whereas diagonalizing the f matrix corresponds to the UHF canonical solution, and the full CI with UHF or ROHF orbitals would be the same, treating f_{ov} via perturbation theory permits more rapid convergence since spin contamination is not introduced into the unperturbed problem.

At first sight we might be tempted to consider $f_{oo} + f_{vv}$ as part of the perturbation, with D_n being composed of diagonal Fock matrix elements. This is the H_0 choice of Carsky and Hubac [21]. However, one of our primary conditions is that our generalized perturbation equations must be invariant to transformations among just the occupied or virtual orbitals, just as CC theory is. This requirement demands that all parts of $f_D = -D_n + f_{oo} + f_{vv}$ be treated equivalently. However, to retain the simplicity of the diagonal case, we can exploit this invariance of the energy and diagonalize the f_D matrix to introduce semicanonical orbitals [30], so that $f_D = -D_n$. The other element we require is that f_{ov} is assumed to be the same order in electron correlation

as W. This is not necessary, and a more general double perturbation treatment can be developed, but this is a convenient choice for many purposes.

Iterating the non-canonical CC equations, and now requiring both T_1 and T_2 contributions,

$$Q_2 D_2 T_2^{(1)} P = Q_2 W P \tag{A.17}$$

$$Q_1 D_1 T_1^{(1)} P = Q_1 f_{ov} P \tag{A.18}$$

from which our generalized MBPT(2) energy is

$$E_2 = \langle W T_2^{(1)} \rangle + \langle f_{ov} T_1^{(1)} \rangle \tag{A.19}$$

Similarly, for MBPT(3)

$$Q_2 D_2 T_2^{(2)} P = Q_2 \left(W T_2^{(1)} + W T_1^{(1)} \right) P \tag{A.20}$$

$$Q_1 D_1 T_1^{(2)} P = Q_1 \left(f_{ov} T_2^{(1)} + W T_2^{(1)} + W T_1^{(1)} \right) P \tag{A.21}$$

$$E_3 = \langle W T_2^{(2)} \rangle + \langle f_{ov} T_1^{(2)} \rangle + \langle W T_1^{(1)} T_1^{(1)} / 2 \rangle \tag{A.22}$$

MBPT(4) introduces effects of T_3 as well. Hence, we have

$$\begin{aligned} Q_2 D_2 T_2^{(3)} P = {} & Q_2 \Big(W T_2^{(2)} + W T_1^{(2)} + f_{ov} T_3^{(2)} + \frac{1}{2} W \left(T_2^{(1)} \right)^2 \\ & + W T_1^{(1)} T_2^{(1)} + f_{ov} T_1^{(1)} T_2^{(1)} + \frac{1}{2} W \left(T_1^{(1)} \right)^2 \Big) P \end{aligned} \tag{A.23}$$

$$\begin{aligned} Q_1 D_1 T_1^{(3)} P = {} & Q_1 \Big(W T_2^{(2)} + W T_1^{(2)} + f_{ov} T_2^{(2)} + W T_3^{(2)} + W T_1^{(1)} T_2^{(1)} \\ & + \frac{1}{2} W \left(T_1^{(1)} \right)^2 + \frac{1}{2} \left(T_1^{(1)} \right)^2 \Big) P \end{aligned} \tag{A.24}$$

where

$$Q_3 D_3 T_3^{(2)} P = Q_3 W T_2^{(1)} P \tag{A.25}$$

This results in

$$E_4 = \langle W T_2^{(3)} \rangle + \langle f_{ov} T_1^{(3)} \rangle + \langle W T_1^{(2)} T_1^{(1)} \rangle \tag{A.26}$$

The fourth order energy excluding triple excitations, SDQ-MBPT(4), is obtained by removing the contributions of $T_3^{(2)}$ in Eqns. (A.23) and (A.24).

Clearly, generalization of the above to any order is straightforward. Requiring the full $T_2^{(3)}$ and $T_1^{(3)}$ amplitudes to evalute E_4 is an unnecessary complication, however, since the E_4 expressions can be simplified via the 2n rule of MBPT as used by Bartlett and coworkers [31, 32].

We know from MBPT that for $V = f_{ov} + W$, $R_0 = (E_0 - H_0)^{-1}$, and $Q = \sum_n Q_n D_n^{-1} Q_n$, we have

$$\begin{aligned} E_4 &= \langle VR_0VR_0VR_0V\rangle_L = \langle 0|V|\phi^{(3)}\rangle_L \\ &= \langle \phi^{(2)}|E_0 - H_0|\phi^{(2)}\rangle_L \end{aligned} \tag{A.27}$$

where

$$\phi_L^{(2)} = \left[Q_2T_2^{(2)} + Q_1T_1^{(2)} + Q_3T_3^{(2)} + Q_2T_1^{(1)}T_1^{(1)}/2 + Q_3T_1^{(1)}T_2^{(1)} + Q_4T_2^{(1)}T_2^{(1)}/2\right]|0\rangle \tag{A.28}$$

Notice the last three terms are linked but disconnected. Readily, one can see that $\langle 0|V|\phi^{(2)}\rangle_L$ gives the same expression as in Eqn. (A.22), since triple and higher excitations do not contribute.

Using Eqn. (A.28)

$$\begin{aligned} E_4 &= \langle T_2^{(2)\dagger}D_2T_2^{(2)}\rangle + \langle T_1^{(2)\dagger}D_1T_1^{(2)}\rangle + \langle T_3^{(2)\dagger}D_3T_3^{(2)}\rangle + \frac{1}{2}\langle T_2^{(2)\dagger}D_2T_1^{(1)}T_1^{(1)}\rangle \\ &+\frac{1}{2}\langle T_1^{(1)\dagger}T_1^{(1)\dagger}D_2T_2^{(2)}\rangle + \frac{1}{4}\langle T_1^{(1)\dagger}T_1^{(1)\dagger}D_2T_1^{(1)}T_1^{(1)}\rangle_L + \langle T_3^{(2)\dagger}D_3T_1^{(1)}T_2^{(1)}\rangle \\ &+\langle T_1^{(1)\dagger}T_2^{(1)\dagger}D_3T_3^{(2)}\rangle + \langle T_1^{(1)\dagger}T_2^{(1)\dagger}D_3T_1^{(1)}T_2^{(1)}\rangle_L + \frac{1}{4}\langle T_2^{(1)\dagger}T_2^{(1)\dagger}D_4T_2^{(1)}T_2^{(1)}\rangle_L \end{aligned} \tag{A.29}$$

The limitation to linked terms applies to some of the non-linear terms. Hence, *most* of the evaluation of E_4 requires simply "squaring" the appropriate T amplitude, e.g. $\langle T_2^{(2)\dagger} D_2 T_2^{(2)} \rangle = \sum_{\substack{i>j \\ a>b}} |t_{ij}^{ab}|^2 (f_{ii} + f_{jj} - f_{aa} - f_{bb})$, where the f_{pp} refers to the diagonal elements of the Fock matrix in the semicanonical basis.

A little inspection and use of the factorization theorem, which in the D_4 case gives $\frac{D_4}{D_2 D_2'} = \frac{1}{D_2} + \frac{1}{D_2'}$, will demonstrate the equivalence between Eqn. (A.26) and Eqn. (A.29). A more detailed demonstration of this equivalence is given in the next section. The non-linear parts of $T_2^{(3)}$ and $T_1^{(3)}$, given by $T_{2NL}^{(3)}$ and $T_{1NL}^{(3)}$ in Eqns. (A.23) and (A.24), represent only connected pieces of the third-order wavefunction; the necessary disconnected pieces contained in Eqn. (A.29) arise from $\langle W T_1^{(2)} T_1^{(1)} \rangle$, which also contributes a piece to $\langle T_1^{(2)\dagger} D_1 T_1^{(2)} \rangle$. Hence, alternatively, we can evalute

$$\begin{aligned} E_4 \;=\; & \langle T_2^{(2)\dagger} D_2 T_2^{(2)} \rangle + \langle T_1^{(2)\dagger} D_1 T_1^{(2)} \rangle + \langle T_3^{(2)\dagger} D_3 T_3^{(2)} \rangle \\ & + \langle W T_{2NL}^{(3)} \rangle + \langle f_{ov} T_{1NL}^{(3)} \rangle + \langle T_2^{(1)\dagger} \left(D_1 T_1^{(2)} \right) T_1^{(1)} \rangle \\ & + \langle T_1^{(1)\dagger} f_{ov} T_2^{(2)} \rangle \end{aligned} \tag{A.30}$$

all terms of which depend solely on T amplitudes of first and second order. It is important to note that the D_1 in the sixth term is associated with $T_1^{(2)}$, and that the last term arises from a linear part of $T_1^{(3)}$ not accounted for in the first three terms of Eqn. (A.30).

A.2 Equivalence Between Expressions for the MBPT(4) Energy

In this section we expand on the equivalence of the MBPT(4) energy expressions without use of the third order amplitudes (Eqns. (A.26) and (A.29)). Recalling the equations for the perturbation theory amplitudes and energies (Eqns. (A.18) to

(A.26)), we substitute for the third order amplitudes in the fourth order energy as follows:

$$\begin{aligned}
\langle WT_2^{(3)}\rangle &= P\frac{W}{D_2}\Big[Q_2WQ_2T_2^{(2)} + Q_2WQ_1T_1^{(2)} + Q_2f_{ov}Q_3T_3^{(2)} \\
&\quad + \frac{1}{2}Q_2WQ_2\left(T_2^{(1)}\right)^2 + Q_2WQ_1T_1^{(1)}Q_2T_2^{(1)} + Q_2f_{ov}Q_1T_1^{(1)}Q_2T_2^{(1)} \\
&\quad + \frac{1}{2}Q_2WQ_1\left(T_1^{(1)}\right)^2\Big]P \\
&= T_2^{(1)\dagger}WT_2^{(2)} + T_2^{(1)\dagger}WT_1^{(2)} + T_2^{(1)\dagger}f_{ov}T_3^{(2)} + T_2^{(1)\dagger}WT_3^{(2)} \\
&\quad + \frac{1}{2}T_2^{(1)\dagger}W\left(T_2^{(1)}\right)^2 + T_2^{(1)\dagger}WT_1^{(1)}T_2^{(1)} + T_2^{(1)\dagger}f_{ov}T_1^{(1)}T_2^{(1)} \\
&\quad + \frac{1}{2}T_2^{(1)\dagger}W\left(T_1^{(1)}\right)^2 \qquad \text{(A.31)}
\end{aligned}$$

$$\begin{aligned}
\langle f_{ov}T_1^{(3)}\rangle &= P\frac{f_{ov}}{D_1}\Big[Q_1WT_2^{(2)} + Q_1WQ_1T_1^{(2)} + Q_1f_{ov}Q_2T_2^{(2)} + Q_1WQ_3T_3^{(2)} \\
&\quad + Q_1WQ_3\left(T_1^{(1)}T_2^{(1)}\right) + \frac{1}{2}Q_1WQ_2\left(T_1^{(1)}\right)^2 + \frac{1}{2}Q_1f_{ov}Q_1\left(T_1^{(1)}\right)^2\Big]P \\
&= T_1^{(1)\dagger}WT_2^{(2)} + T_1^{(1)\dagger}WT_1^{(2)} + T_1^{(1)\dagger}f_{ov}T_2^{(2)} + T_1^{(1)\dagger}WT_3^{(2)} \\
&\quad + T_1^{(1)\dagger}WQ_3\left(T_1^{(1)}T_2^{(1)}\right) + \frac{1}{2}T_1^{(1)\dagger}WQ_2\left(T_1^{(1)}\right)^2 + \frac{1}{2}T_1^{(1)\dagger}f_{ov}\left(T_1^{(1)}\right)^2 \\
&\qquad \text{(A.32)}
\end{aligned}$$

We can now label the terms from each of these energy pieces. For the time being, we will deal only with these two contributions to the energy. We will discuss the terms arising from $\langle WT_1^{(2)}T_1^{(1)}\rangle$ later in this section. The terms from the equations above are given in Table A.1.

Table A.1. Terms[a] from the CC expansion of the MBPT(4) energy.

Terms from $T_2^{(3)}$	Terms from $T_1^{(3)}$
1) $T_2^{(1)\dagger} W T_2^{(2)}$	1) $T_1^{(1)\dagger} W T_2^{(2)}$
2) $T_2^{(1)\dagger} W T_1^{(2)}$	2) $T_1^{(1)\dagger} W T_1^{(2)}$
3) $T_2^{(1)\dagger} f_{ov} T_3^{(2)}$	3) $T_1^{(1)\dagger} f_{ov} T_2^{(2)}$
4) $T_2^{(1)\dagger} W T_3^{(2)}$	4) $T_1^{(1)\dagger} W T_3^{(2)}$
5) $\frac{1}{2} T_2^{(1)\dagger} W \left(T_2^{(1)}\right)^2$	5) $T_1^{(1)\dagger} W Q_3 \left(T_1^{(1)} T_2^{(1)}\right)$
6) $T_2^{(1)\dagger} W T_1^{(1)} T_2^{(1)}$	6) $\frac{1}{2} T_1^{(1)\dagger} W Q_2 \left(T_1^{(1)}\right)^2$
7) $T_2^{(1)\dagger} f_{ov} T_1^{(1)} T_2^{(1)}$	7) $\frac{1}{2} T_1^{(1)\dagger} f_{ov} \left(T_1^{(1)}\right)^2$
8) $\frac{1}{2} T_2^{(1)\dagger} W \left(T_1^{(1)}\right)^2$	

[a]All terms arise from only the connected pieces of the third-order wavefunction.

The alternate expressions arising from the use of the 2n rule of perturbation theory leads to Eqns (A.27) to (A.29). Labelling each of the terms from Eqn. (A.29) gives us Table A.2.

The MBPT expansion for E(4) has all the energy terms. We will now see how each of the terms for the MBPT expansion match up with the terms from the CC expansion. Keep in mind that we still have not dealt with the terms from $\langle W T_1^{(2)} T_1^{(1)} \rangle$. Also, each of the terms in Table A.1 represent contributions from connected pieces of the third-order wavefunction.

Using the (1) terms from $T_1^{(3)}$ and $T_2^{(3)}$:

$$\begin{aligned} T_2^{(1)\dagger} W T_2^{(2)} + T_1^{(1)\dagger} W T_2^{(2)} &= \left[T_2^{(1)\dagger} W + T_1^{(1)\dagger} W \right] T_2^{(2)} \\ &= \frac{1}{D_2} \left[T_2^{(1)\dagger} W + T_1^{(1)\dagger} W \right] D_2 T_2^{(2)} \\ &= T_2^{(2)\dagger} D_2 T_2^{(2)} \end{aligned} \tag{A.33}$$

which accounts for (a) of the MBPT expansion.

Table A.2. Terms from the MBPT expansion of the MBPT(4) energy.

Terms from the MBPT expansion	
a)	$\langle T_2^{(2)\dagger} D_2 T_2^{(2)} \rangle$
b)	$\langle T_1^{(2)\dagger} D_1 T_1^{(2)} \rangle$
c)	$\langle T_3^{(2)\dagger} D_3 T_3^{(2)} \rangle$
d)	$\frac{1}{4} \langle T_1^{(1)\dagger} T_1^{(1)\dagger} D_2 T_1^{(1)} T_1^{(1)} \rangle_L$
e)	$\langle T_1^{(1)\dagger} T_2^{(1)\dagger} D_3 T_1^{(1)} T_2^{(1)} \rangle_L$
f)	$\frac{1}{4} \langle T_2^{(1)\dagger} T_2^{(1)\dagger} D_4 T_2^{(1)} T_2^{(1)} \rangle_L$
g)	$\frac{1}{2} T_2^{(2)\dagger} D_2 T_1^{(1)} T_1^{(1)} \rangle$
h)	$\frac{1}{2} \langle T_1^{(1)\dagger} T_1^{(1)\dagger} D_2 T_2^{(2)} \rangle$
i)	$\langle T_3^{(2)\dagger} D_3 T_1^{(1)} T_2^{(1)} \rangle$
j)	$\langle T_1^{(1)\dagger} T_2^{(1)\dagger} D_3 T_3^{(2)} \rangle$

Factorizing (e) of the MBPT expansion:

$$\langle T_1^{(1)\dagger} T_1^{(2)\dagger} D_3 T_1^{(1)} T_2^{(1)} \rangle_L$$

$$\frac{D_3}{D_1 D_2} = \frac{D_1 + D_2}{D_1 D_2} = \frac{1}{D_1} + \frac{1}{D_2}$$

$$\langle f_{ov} W \left(\frac{1}{D_1} + \frac{1}{D_2} \right) T_1^{(1)} T_2^{(1)} \rangle = \langle T_1^{(1)\dagger} W T_1^{(1)} T_2^{(1)} \rangle + \langle T_2^{(1)\dagger} f_{ov} T_1^{(1)} T_2^{(1)} \rangle \qquad \text{(A.34)}$$

The first term of the last equation corresponds to (5) of $T_1^{(3)}$, while the second term of the last equation corresponds to (7) of $T_2^{(3)}$.

Using the (4) term from $T_2^{(3)}$:

$$\begin{aligned} T_2^{(1)\dagger} W T_3^{(2)} &= \frac{T_2^{(1)\dagger} W}{D_3} D_3 T_3^{(2)} \\ &= T_3^{(2)\dagger} D_3 T_3^{(2)} \end{aligned} \qquad \text{(A.35)}$$

which accounts for (c) of the MBPT expansion.

Factorizing (d) of the MBPT expansion:

$$\frac{1}{4}\langle T_1^{(1)\dagger} T_1^{(1)\dagger} D_2 T_1^{(1)} T_1^{(1)} \rangle_L$$

$$\frac{D_2}{D_1 D_1'} = \frac{D_1 + D_1'}{D_1 D_1'} = \frac{1}{D_1} + \frac{1}{D_1'}$$

$$\begin{aligned} \frac{1}{4}\langle f_{ov} f_{ov} \left(\frac{1}{D_1} + \frac{1}{D_1'}\right) T_1^{(1)} T_1^{(1)} \rangle &= \frac{1}{4}\langle T_1^{(1)\dagger} f_{ov} T_1^{(1)} T_1^{(1)} \rangle + \frac{1}{4}\langle T_1^{(1)\dagger} f_{ov} T_1^{(1)} T_1^{(1)} \rangle \\ &= \frac{1}{2}\langle T_1^{(1)\dagger} f_{ov} \left(T_1^{(1)}\right)^2 \rangle \end{aligned} \tag{A.36}$$

which accounts for (7) of $T_1^{(3)}$.

Manipulating (i) from the MBPT expansion:

$$\langle T_3^{(2)\dagger} D_3 T_1^{(1)} T_2^{(1)} \rangle$$

$$T_3^{(2)\dagger} = \frac{1}{D_3} T_2^{(1)\dagger} W$$

$$\left(\frac{T_2^{(1)\dagger} W}{D_3}\right) D_3 T_1^{(1)} T_2^{(1)} = T_2^{(1)\dagger} W T_1^{(1)} T_2^{(1)} \tag{A.37}$$

which accounts for (6) from $T_2^{(3)}$.

Factorizing (f) from the MBPT expansion:

$$\frac{1}{4}\langle T_2^{(1)\dagger} T_2^{(1)\dagger} D_4 T_2^{(1)} T_2^{(1)} \rangle_L$$

$$\frac{D_4}{D_2 D_2'} = \frac{D_2 + D_2'}{D_2 D_2'} = \frac{1}{D_2} + \frac{1}{D_2'}$$

$$\frac{1}{4}\langle WW\left(\frac{1}{D_2}+\frac{1}{D_2'}\right)T_2^{(1)}T_2^{(1)}\rangle = \frac{1}{4}\langle T_2^{(1)\dagger}WT_2^{(1)}T_2^{(1)}\rangle + \frac{1}{4}\langle T_2^{(1)\dagger}WT_2^{(1)}T_2^{(1)}\rangle$$

$$= \frac{1}{2}\langle T_2^{(1)\dagger}W\left(T_2^{(1)}\right)^2\rangle \qquad \text{(A.38)}$$

which accounts for (5) from $T_2^{(3)}$.

Factorizing (j) from the MBPT expansion:

$$\langle T_1^{(1)\dagger}T_2^{(1)\dagger}D_3T_3^{(2)}\rangle$$

$$\frac{D_3}{D_1D_2} = \frac{D_1+D_2}{D_1D_2} = \frac{1}{D_1}+\frac{1}{D_2}$$

$$\langle f_{ov}W\left(\frac{1}{D_1}+\frac{1}{D_2}\right)T_3^{(2)}\rangle = \langle T_1^{(1)\dagger}WT_3^{(2)}\rangle + \langle T_2^{(1)\dagger}f_{ov}T_3^{(2)}\rangle \qquad \text{(A.39)}$$

The first term of the last equation corresponds to (4) of $T_1^{(3)}$ and the second term corresponds to (3) of $T_2^{(3)}$.

Using (6) from $T_1^{(3)}$ and (8) from $T_2^{(3)}$:

$$\frac{1}{2}T_2^{(1)\dagger}W\left(T_1^{(1)}\right)^2\frac{1}{2}T_1^{(1)\dagger}W\left(T_1^{(1)}\right)^2 = \frac{1}{2}\left[T_2^{(1)\dagger}W+T_1^{(1)\dagger}W\right]\left(T_1^{(1)}\right)^2$$

$$= \frac{1}{2}\frac{1}{2}\left[T_2^{(1)\dagger}W+T_1^{(1)\dagger}W\right]D_2\left(T_1^{(1)}\right)^2$$

$$= \frac{1}{2}T_2^{(2)\dagger}D_2\left(T_1^{(1)}\right)^2 \qquad \text{(A.40)}$$

which accounts for (g) of the MBPT expansion.

Factorizing (h) from the MBPT expansion:

$$\frac{1}{2}\langle T_1^{(1)\dagger}T_1^{(1)\dagger}D_2T_2^{(2)}\rangle$$

$$\frac{D_2}{D_1 D_1'} = \frac{D_1 + D_1'}{D_1 D_1'} = \frac{1}{D_1} + \frac{1}{D_1'}$$

$$\begin{aligned} \frac{1}{2}\langle f_{ov} f_{ov} \left(\frac{1}{D_1} + \frac{1}{D_1'}\right) T_2^{(2)} \rangle &= \frac{1}{2}\langle T_1^{(1)\dagger} f_{ov} T_2^{(2)} \rangle + \frac{1}{2}\langle T_1^{(1)\dagger} f_{ov} T_2^{(2)} \rangle \\ &= \langle T_1^{(1)\dagger} f_{ov} T_2^{(2)} \rangle \end{aligned} \tag{A.41}$$

which accounts for (3) from $T_1^{(3)}$.

Manipulating the (b) term of the MBPT expansion:

$$\langle T_1^{(2)\dagger} D_1 T_1^{(2)} \rangle$$

Since

$$T_1^{(2)\dagger} = \left[T_2^{(1)\dagger} f_{ov} + T_1^{(2)\dagger} W + T_1^{(1)\dagger} W \right] \frac{1}{D_1} \tag{A.42}$$

Then substituting for $T_1^{(2)\dagger}$ we get

$$\langle T_1^{(2)\dagger} D_1 T_1^{(2)} \rangle = \langle T_2^{(1)\dagger} f_{ov} T_1^{(2)} \rangle + \langle T_2^{(1)\dagger} W T_1^{(2)} \rangle + \langle T_1^{(1)\dagger} W T_1^{(2)} \rangle \tag{A.43}$$

The second term of the last equation accounts for (2) of $T_2^{(3)}$, and the third term accounts for (2) of $T_1^{(3)}$. However, we cannot account for the first term of the last equation using the terms in Table A.1.

At this point, we have accounted for all the terms in the MBPT and CC expansions which involve connected pieces of the third-order wavefunction. We now examine the remaining CC energy term, $\langle W T_1^{(2)} T_1^{(1)} \rangle$. If we factorize $\langle W T_1^{(2)} T_1^{(1)} \rangle$, then

$$\frac{1}{D_1 D_1'} \times \frac{D_2}{D_2} = \frac{D_2}{D_1 D_1'} \times \frac{1}{D_2} = \left(\frac{1}{D_1} + \frac{1}{D_1'}\right) \frac{1}{D_2}$$

$$\langle W T_1^{(2)} T_1^{(1)} \rangle = \langle \frac{W}{D_2} f_{ov} T_1^{(2)} \rangle + \langle \frac{W}{D_2} \left[f_{ov} T_2^{(1)} + W T_2^{(1)} + W T_1^{(1)} \right] T_1^{(1)} \rangle$$

$$= \langle T_2^{(1)\dagger} f_{ov} T_1^{(2)} \rangle + \langle \Big[T_2^{(1)\dagger} f_{ov} T_2^{(1)} T_1^{(1)} + T_2^{(1)\dagger} W T_2^{(1)} T_1^{(1)} + T_2^{(1)\dagger} W \left(T_1^{(1)} \right)^2 \Big] \rangle \tag{A.44}$$

The first term of the last equation accounts for the remaining term of (b) in the MBPT expansion. The remaining terms all appear to be the same as terms (6) - (8) for $T_2^{(3)}$ in Table A.1. These terms, however, represent the disconnected pieces of the $T_2^{(3)}$ part of the wavefunction. Therefore, these three terms as found in the expansion for $T_2^{(3)}$ represent the connected parts of the wavefunction, while their appearance in $\langle W T_1^{(2)} T_1^{(1)} \rangle$ represent the disconnected parts of the wavefunction.

With all the terms accounted for, we can now express the fourth order energy as

$$\begin{aligned} E_4 &= \langle T_2^{(2)\dagger} D_2 T_2^{(2)} \rangle + \langle T_1^{(2)\dagger} D_1 T_1^{(2)} \rangle + \langle T_3^{(2)\dagger} D_3 T_3^{(2)} \rangle \\ &\quad + \langle W T_2^{(3)}{}_{NL} \rangle + \langle f_{ov} T_1^{(3)}{}_{NL} \rangle + \langle W T_1^{(2)} T_1^{(1)} \rangle \\ &\quad - \langle T_2^{(1)\dagger} f_{ov} T_1^{(2)} \rangle + \langle T_1^{(1)\dagger} f_{ov} T_2^{(2)} \rangle \end{aligned} \tag{A.45}$$

where the second-to-last term in Eqn. (A.45) accounts for the fact that this term appears in both the T_1 "squared" term and the $\langle W T_1^{(2)} T_1^{(1)} \rangle$ terms and is hence overcounted, and the last term is not present in any of the "squared" terms and needs to be added. Eqn. (A.45) is equivalent to the expression for the fourth-order energy given in Chapter 2. Alternatively, we can take the expansion of $W T_1^{(2)} T_1^{(1)}$ and represent it as

$$\langle W T_1^{(2)} T_1^{(1)} \rangle = \langle T_2^{(1)\dagger} f_{ov} T_1^{(2)} \rangle + \langle T_2^{(1)\dagger} \left(D_1 T_1^{(2)} \right) T_1^{(1)} \rangle \tag{A.46}$$

which then allows us to give the E_4 energy as shown in Eqn. (A.30).

APPENDIX B

ROHF COUPLED-PERTURBED HF (CPHF) DERIVATION

This appendix deals with the derivation of the additional elements required for solution of the ROHF CPHF equations. The end result gives the terms required for construction of the A matrix of CPHF theory. These additional terms have been incorporated in the *ab initio* program system ACES II [33] to provide for correlated analytical gradients. Currently, these analytical gradients are available for MBPT(2) and CCSD.

ROHF conditions:

$$ {}^{\alpha}f_{AI} + {}^{\beta}f_{AI} = 0 \tag{B.1} $$

$$ {}^{\alpha}f_{A1} = 0 \tag{B.2} $$

$$ {}^{\beta}f_{1I} = 0 \tag{B.3} $$

First condition: ${}^{\alpha}f_{AI} + {}^{\beta}f_{AI} = 0$

$$ \frac{\partial\, {}^{\alpha}f_{AI}}{\partial\chi} + \frac{\partial\, {}^{\beta}f_{AI}}{\partial\chi} = 0 \tag{B.4} $$

$$ {}^{\alpha}f_{AI} = \sum_{\mu\nu} C_{\mu A}\, {}^{\alpha}f_{\mu\nu} C_{\nu I} \tag{B.5} $$

$$ \frac{\partial\, {}^{\alpha}f_{AI}}{\partial\chi} + \frac{\partial\, {}^{\beta}f_{AI}}{\partial\chi} = \sum_{\mu\nu} \left[\frac{\partial\, C_{\mu A}}{\partial\chi}\, {}^{\alpha}f_{\mu\nu} C_{\nu I} + C_{\mu A} \frac{\partial\, {}^{\alpha}f_{\mu\nu}}{\partial\chi} C_{\nu I} + C_{\mu A}\, {}^{\alpha}f_{\mu\nu} \frac{\partial\, C_{\nu I}}{\partial\chi} \right] + $$

$$\sum_{\mu\nu}\left[\frac{\partial C_{\mu A}}{\partial \chi}\,{}^{\beta}f_{\mu\nu}C_{\nu I}+C_{\mu A}\frac{\partial\,{}^{\beta}f_{\mu\nu}}{\partial \chi}C_{\nu I}+C_{\mu A}\,{}^{\beta}f_{\mu\nu}\frac{\partial C_{\nu I}}{\partial \chi}\right] \quad \text{(B.6)}$$

but,

$$\frac{\partial C_{\mu A}}{\partial \chi}=\sum_{P}U^{\chi}_{PA}C_{\mu P} \quad \text{(B.7)}$$

so

$$\begin{aligned}0 \;=\; &\sum_{\mu\nu}\left[\sum_{P}U^{\chi}_{PA}C_{\mu P}\,{}^{\alpha}f_{\mu\nu}C_{\nu I}+C_{\mu A}\frac{\partial\,{}^{\alpha}f_{\mu\nu}}{\partial \chi}C_{\nu I}+\sum_{P}U^{\chi}_{PI}C_{\nu P}\,{}^{\alpha}f_{\mu\nu}C_{\mu A}\right]+\\ &\sum_{\mu\nu}\left[\sum_{P}U^{\chi}_{PA}C_{\mu P}\,{}^{\beta}f_{\mu\nu}C_{\nu I}+C_{\mu A}\frac{\partial\,{}^{\beta}f_{\mu\nu}}{\partial \chi}C_{\nu I}+\sum_{P}U^{\chi}_{PI}C_{\nu P}\,{}^{\beta}f_{\mu\nu}C_{\mu A}\right] \quad \text{(B.8)}\end{aligned}$$

Summing over $\mu\nu$ gives us

$$\left[\sum_{P}U^{\chi}_{PA}\,{}^{\alpha}f_{PI}+{}^{\alpha}f^{\chi}_{AI}+\sum_{P}U^{\chi}_{PI}\,{}^{\alpha}f_{PA}\right]+\left[\sum_{P}U^{\chi}_{PA}\,{}^{\beta}f_{PI}+{}^{\beta}f^{\chi}_{AI}+\sum_{P}U^{\chi}_{PI}\,{}^{\beta}f_{PA}\right] \quad \text{(B.9)}$$

where

$${}^{\alpha}f^{\chi}_{AI}=\frac{\partial\,{}^{\alpha}f_{AI}}{\partial \chi}$$

$${}^{\beta}f^{\chi}_{AI}=\frac{\partial\,{}^{\beta}f_{AI}}{\partial \chi}$$

We can further consolidate the expression to

$$\sum_{P}U^{\chi}_{PA}\left({}^{\alpha}f_{PI}+{}^{\beta}f_{PI}\right)+\sum_{P}U^{\chi}_{PI}\left({}^{\alpha}f_{AP}+{}^{\beta}f_{AP}\right)+{}^{\alpha}f^{\chi}_{AI}+{}^{\beta}f^{\chi}_{AI}=0 \quad \text{(B.10)}$$

Since P can run over all types of orbitals (doubly occupied, singly occupied, and virtual), we can break the summation over P down to these types:

$$\sum_P U^X_{PA}\left({}^\alpha f_{PI} + {}^\beta f_{PI}\right) = \sum_J U^X_{JA}\left({}^\alpha f_{JI} + {}^\beta f_{JI}\right) + \tag{B.11}$$

$$\sum_1 U^X_{1A}\left({}^\alpha f_{1I} + {}^\beta f_{1I}\right) + \tag{B.12}$$

$$\sum_B U^X_{BA}\left({}^\alpha f_{BI} + {}^\beta f_{BI}\right) \tag{B.13}$$

Recalling our ROHF conditions, we can see the term given by Eqn. (B.13) disappears because of the first ROHF condition (Eqn. (B.1)). The β part of the term given by Eqn. (B.12) disappears because of the last ROHF condition (Eqn. (B.3)). We now have:

$$\sum_P U^X_{PA}\left({}^\alpha f_{PI} + {}^\beta f_{PI}\right) = \sum_J U^X_{JA}\left({}^\alpha f_{JI} + {}^\beta f_{JI}\right) + \sum_1 U^X_{1A}\,{}^\alpha f_{1I} \tag{B.14}$$

Expanding the second summation of equation (B.10) gives

$$\sum_P U^X_{PI}\left({}^\alpha f_{AP} + {}^\beta f_{AP}\right) = \sum_J U^X_{JI}\left({}^\alpha f_{AJ} + {}^\beta f_{AJ}\right) + \tag{B.15}$$

$$\sum_1 U^X_{1I}\left({}^\alpha f_{A1} + {}^\beta f_{A1}\right) + \tag{B.16}$$

$$\sum_B U^X_{BI}\left({}^\alpha f_{AB} + {}^\beta f_{AB}\right) \tag{B.17}$$

The term given by equation (B.15) disappears because of the first ROHF condition. The α piece of the term given by equation (B.16) disappears because of the second ROHF condition. This yields:

$$\sum_P U^X_{PI}\left({}^\alpha f_{AP} + {}^\beta f_{AP}\right) = \sum_1 U^X_{1I}\,{}^\alpha f_{A1} + \sum_B U^X_{BI}\left({}^\alpha f_{AB} + {}^\beta f_{AB}\right) \tag{B.18}$$

At this stage, let's explore what we know about the U^{χ}'s. We have six classes of U^{χ}'s:

$$\left\{ \begin{matrix} U_{IJ} \\ U_{JI} \end{matrix} \right. \quad \left\{ \begin{matrix} U_{AB} \\ U_{BA} \end{matrix} \right. \quad \left\{ \begin{matrix} U_{12} \\ U_{21} \end{matrix} \right. \quad \left\{ \begin{matrix} U_{1I} \\ U_{I1} \end{matrix} \right. \quad \left\{ \begin{matrix} U_{AI} \\ U_{IA} \end{matrix} \right. \quad \left\{ \begin{matrix} U_{A1} \\ U_{1A} \end{matrix} \right.$$

If we are dealing solely with a particular subspace (doubly occupied, singly occupied, or virtual), the energy is invariant to arbitrary rotations within the subspace. We can therefore define the U^{χ}'s for these subspaces as fits our needs. With this in mind, we define the following U^{χ}'s:

$$\begin{aligned} U^{\chi}_{IJ} &= -\frac{1}{2} S^{\chi}_{IJ} \\ U^{\chi}_{AB} &= -\frac{1}{2} S^{\chi}_{AB} \\ U^{\chi}_{12} &= -\frac{1}{2} S^{\chi}_{12} \end{aligned} \tag{B.19}$$

where S^{χ} represents the derivative of the overlap matrix S.

These definitions account for three of the classes. Now let's examine the last two terms of equation (B.10).

$${}^{\alpha}f^{\chi}_{AI} = \sum_{\mu\nu} C_{\mu A} \frac{\partial\, {}^{\alpha}f_{\mu\nu}}{\partial \chi} C_{\nu I} \tag{B.20}$$

$${}^{\alpha}f_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma\lambda} D_{\sigma\lambda} \langle \mu\sigma \| \nu\lambda \rangle \tag{B.21}$$

$$\frac{\partial\, {}^{\alpha}f_{\mu\nu}}{\partial \chi} = h^{\chi}_{\mu\nu} + \sum_{\sigma\lambda} \frac{\partial\, D_{\sigma\lambda}}{\partial \chi} \langle \mu\sigma \| \nu\lambda \rangle + \sum_{\sigma\lambda} D_{\sigma\lambda} \frac{\partial \langle \mu\sigma \| \nu\lambda \rangle}{\partial \chi} \tag{B.22}$$

where

$$h^{\chi}_{\mu\nu} = \frac{\partial h_{\mu\nu}}{\partial \chi}$$

$$ {}^{\alpha}f^{\chi}_{AI} = \sum_{\mu\nu}\left[C_{\mu A}h^{\chi}_{\mu\nu}C_{\nu I} + \sum_{\sigma\lambda}\frac{\partial D_{\sigma\lambda}}{\partial\chi}\langle\mu\sigma\|\nu\lambda\rangle C_{\mu A}C_{\nu I} + \sum_{\sigma\lambda}D_{\sigma\lambda}C_{\mu A}C_{\nu I}\langle\mu\sigma\|\nu\lambda\rangle^{\chi}\right] \tag{B.23} $$

where

$$ \langle\mu\sigma\|\nu\lambda\rangle^{\chi} = \frac{\partial\langle\mu\sigma\|\nu\lambda\rangle}{\partial\chi} $$

This leads to the expression

$$ {}^{\alpha}f^{\chi}_{AI} = h^{\chi}_{AI} + \sum_{\sigma\lambda}D^{\chi}_{\sigma\lambda}\langle A\sigma\|I\lambda\rangle + \sum_{\sigma\lambda}D_{\sigma\lambda}\langle A\sigma\|I\lambda\rangle^{\chi} \tag{B.24} $$

$$ \begin{aligned} \sum_{\sigma\lambda}D_{\sigma\lambda}\langle A\sigma\|I\lambda\rangle^{\chi} &= \sum_{\sigma\lambda}\sum_{m}^{\alpha}C_{\sigma m}C_{\lambda m}\langle A\sigma\|I\lambda\rangle^{\chi} + \\ &\quad \sum_{\sigma\lambda}\sum_{n}^{\beta}C_{\sigma n}C_{\lambda n}\langle A\sigma\|I\lambda\rangle^{\chi} \end{aligned} \tag{B.25} $$

$$ \sum_{\sigma\lambda}D_{\sigma\lambda}\langle A\sigma\|I\lambda\rangle^{\chi} = \sum_{m}^{\alpha}\langle Am\|Im\rangle^{\chi} + \sum_{n}^{\beta}\langle An\|In\rangle^{\chi} \tag{B.26} $$

$$ \begin{aligned} \sum_{\sigma\lambda}D^{\chi}_{\sigma\lambda}\langle A\sigma\|I\lambda\rangle &= \sum_{\sigma\lambda}\sum_{m}^{\alpha}\frac{\partial C_{\sigma m}}{\partial\chi}C_{\lambda m}\langle A\sigma\|I\lambda\rangle + \sum_{\sigma\lambda}\sum_{m}^{\alpha}C_{\sigma m}\frac{\partial C_{\lambda m}}{\partial\chi}\langle A\sigma\|I\lambda\rangle + \\ &\quad \sum_{\sigma\lambda}\sum_{n}^{\beta}\frac{\partial C_{\sigma n}}{\partial\chi}C_{\lambda n}\langle A\sigma\|I\lambda\rangle + \sum_{\sigma\lambda}\sum_{n}^{\beta}C_{\sigma n}\frac{\partial C_{\lambda n}}{\partial\chi}\langle A\sigma\|I\lambda\rangle \end{aligned} \tag{B.27} $$

Recalling equation (B.7) and substituting into the last equation we get

$$\sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda}\langle A\sigma\|I\lambda\rangle = \sum_{\sigma\lambda}\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm} C_{\sigma P} C_{\lambda m}\langle A\sigma\|I\lambda\rangle +$$

$$\sum_{\sigma\lambda}\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm} C_{\sigma m} C_{\lambda P}\langle A\sigma\|I\lambda\rangle +$$

$$\sum_{\sigma\lambda}\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn} C_{\sigma P} C_{\lambda n}\langle A\sigma\|I\lambda\rangle +$$

$$\sum_{\sigma\lambda}\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn} C_{\sigma n} C_{\lambda P}\langle A\sigma\|I\lambda\rangle \qquad \text{(B.28)}$$

$$\sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda}\langle A\sigma\|I\lambda\rangle = \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle AP\|Im\rangle + \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle Am\|IP\rangle +$$

$$\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle AP\|In\rangle + \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle An\|IP\rangle \qquad \text{(B.29)}$$

Substituting equations (B.24) and (B.26) into equation (B.29) yields

$$^{\alpha}f^{\chi}_{AI} = h^{\chi}_{AI} + \sum_{m}^{\alpha}\langle Am\|Im\rangle^{\chi} + \sum_{n}^{\beta}\langle An\|In\rangle^{\chi} + \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle AP\|Im\rangle +$$

$$\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle Am\|IP\rangle + \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle AP\|In\rangle + \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle An\|IP\rangle \qquad \text{(B.30)}$$

Solving for $^{\beta}f^{\chi}_{AI}$ will yield a similar expression, except that α and β terms will be reversed. The resulting expression for $^{\beta}f^{\chi}_{AI}$ is:

$$^{\beta}f^{\chi}_{AI} = h^{\chi}_{AI} + \sum_{n}^{\beta}\langle An\|In\rangle^{\chi} + \sum_{m}^{\alpha}\langle Am\|Im\rangle^{\chi} + \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle AP\|In\rangle +$$

$$\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle An\|IP\rangle + \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle AP\|Im\rangle + \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle Am\|IP\rangle \tag{B.31}$$

Substituting equations (B.31), (B.30), (B.18), and (B.10) into the last equation and separating into known and unknown pieces results in the following equation:

$$\begin{aligned}
&\sum_{J} U^{\chi}_{JA}\left({}^{\alpha}f_{JI} + {}^{\beta}f_{JI}\right) + \sum_{1}\left(U^{\chi}_{1A}{}^{\alpha}f_{1I} + U^{\chi}_{1I}{}^{\beta}f_{A1}\right) + \sum_{B} U^{\chi}_{BI}\left({}^{\alpha}f_{AB} + {}^{\beta}f_{AB}\right) + \\
&\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle AP\|Im\rangle_{\alpha\alpha\alpha\alpha} + \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle Am\|IP\rangle_{\alpha\alpha\alpha\alpha} + \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle AP\|In\rangle_{\alpha\beta\alpha\beta} + \\
&\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle An\|IP\rangle_{\alpha\beta\alpha\beta} + \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle AP\|In\rangle_{\beta\beta\beta\beta} + \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle An\|IP\rangle_{\beta\beta\beta\beta} + \\
&\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle AP\|Im\rangle_{\beta\alpha\beta\alpha} + \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle Am\|IP\rangle_{\beta\alpha\beta\alpha} \\
= \quad &-\left[h^{\chi}_{AI} + h^{\chi}_{AI} + \sum_{m}^{\alpha}\langle Am\|Im\rangle^{\chi}_{\alpha\alpha\alpha\alpha} + \sum_{n}^{\beta}\langle An\|In\rangle^{\chi}_{\alpha\beta\alpha\beta} + \sum_{n}^{\beta}\langle An\|In\rangle^{\chi}_{\beta\beta\beta\beta} + \right. \\
&\left.\sum_{m}^{\alpha}\langle Am\|Im\rangle^{\chi}_{\beta\alpha\beta\alpha}\right]
\end{aligned} \tag{B.32}$$

From the discussion of the U^{χ}'s before, we have three classes which need to be determined. We therefore need to solve three simultaneous equations. Let's derive the next one from the second ROHF condition (Eqn. (B.2)).

$$0 = \frac{\partial\, {}^{\alpha}f_{A1}}{\partial\chi} = \sum_{\mu\nu}\left[\frac{\partial C_{\mu A}}{\partial\chi}\,{}^{\alpha}f_{\mu\nu}C_{\nu 1} + C_{\mu A}\frac{\partial\, {}^{\alpha}f_{\mu\nu}}{\partial\chi}C_{\nu 1} + C_{\mu A}{}^{\alpha}f_{\mu\nu}\frac{\partial C_{\nu 1}}{\partial\chi}\right] \tag{B.33}$$

$${}^{\alpha}f^{\chi}_{A1} = \sum_{\mu\nu} C_{\mu A}\frac{\partial\, {}^{\alpha}f_{\mu\nu}}{\partial\chi}C_{\nu 1} \tag{B.34}$$

$$ {}^{\alpha}f_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma\lambda} D_{\sigma\lambda}\langle\mu\sigma\|\nu\lambda\rangle \tag{B.35} $$

$$ \frac{\partial\, {}^{\alpha}f_{\mu\nu}}{\partial\chi} = \frac{\partial h_{\mu\nu}}{\partial\chi} + \sum_{\sigma\lambda}\frac{\partial D_{\sigma\lambda}}{\partial\chi}\langle\mu\sigma\|\nu\lambda\rangle + \sum_{\sigma\lambda} D_{\sigma\lambda}\frac{\partial\langle\mu\sigma\|\nu\lambda\rangle}{\partial\chi} \tag{B.36} $$

$$ \frac{\partial\, {}^{\alpha}f_{\mu\nu}}{\partial\chi} = h^{\chi}_{\mu\nu} + \sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda}\langle\mu\sigma\|\nu\lambda\rangle + \sum_{\sigma\lambda} D_{\sigma\lambda}\langle\mu\sigma\|\nu\lambda\rangle^{\chi} \tag{B.37} $$

$$ {}^{\alpha}f^{\chi}_{A1} = \sum_{\mu\nu}\left[C_{\mu A}h^{\chi}_{\mu\nu}C_{\nu 1} + \sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda}\langle\mu\sigma\|\sigma\lambda\rangle + \sum_{\sigma\lambda} D_{\sigma\lambda}\langle\mu\sigma\|\nu\lambda\rangle^{\chi}C_{\mu A}C_{\nu 1}\right] \tag{B.38} $$

$$ {}^{\alpha}f^{\chi}_{A1} = h^{\chi}_{A1} + \sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda}\langle A\sigma\|1\lambda\rangle + \sum_{\sigma\lambda} D_{\sigma\lambda}\langle A\sigma\|1\lambda\rangle^{\chi} \tag{B.39} $$

$$ \sum_{\sigma\lambda} D_{\sigma\lambda}\langle A\sigma\|1\lambda\rangle^{\chi} = \sum_{\sigma\lambda}\sum_{m}^{\alpha} C_{\sigma m}C_{\lambda m}\langle A\sigma\|1\lambda\rangle^{\chi}_{\alpha\alpha\alpha\alpha} + \sum_{\sigma\lambda}\sum_{n}^{\beta} C_{\sigma n}C_{\lambda n}\langle A\sigma\|1\lambda\rangle^{\chi}_{\alpha\beta\alpha\beta} \tag{B.40} $$

$$ \sum_{\sigma\lambda} D_{\sigma\lambda}\langle A\sigma\|1\lambda\rangle^{\chi} = \sum_{m}^{\alpha}\langle Am\|1m\rangle^{\chi}_{\alpha\alpha\alpha\alpha} + \sum_{n}^{\beta}\langle An\|1n\rangle^{\chi}_{\alpha\beta\alpha\beta} \tag{B.41} $$

$$ \begin{aligned} \sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda}\langle A\sigma\|1\lambda\rangle \;=\; & \sum_{\sigma\lambda}\sum_{m}^{\alpha}\frac{\partial C_{\sigma m}}{\partial\chi}C_{\lambda m}\langle A\sigma\|1\lambda\rangle_{\alpha\alpha\alpha\alpha} + \\ & \sum_{\sigma\lambda}\sum_{m}^{\alpha} C_{\sigma m}\frac{\partial C_{\lambda m}}{\partial\chi}\langle A\sigma\|1\lambda\rangle_{\alpha\alpha\alpha\alpha} + \\ & \sum_{\sigma\lambda}\sum_{n}^{\beta}\frac{\partial C_{\sigma n}}{\partial\chi}C_{\lambda n}\langle A\sigma\|1\lambda\rangle_{\alpha\beta\alpha\beta} + \\ & \sum_{\sigma\lambda}\sum_{n}^{\beta} C_{\sigma n}\frac{\partial C_{\lambda n}}{\partial\chi}\langle A\sigma\|1\lambda\rangle_{\alpha\beta\alpha\beta} \end{aligned} \tag{B.42} $$

Recalling equation (B.7) and substituting into the last equation,

$$\begin{aligned}\sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda}\langle A\sigma\|1\lambda\rangle &= \sum_{\sigma\lambda}\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm} C_{\sigma P} C_{\lambda m}\langle A\sigma\|1\lambda\rangle_{\alpha\alpha\alpha\alpha} + \\ &\sum_{\sigma\lambda}\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm} C_{\sigma m} C_{\lambda P}\langle A\sigma\|1\lambda\rangle_{\alpha\alpha\alpha\alpha} + \\ &\sum_{\sigma\lambda}\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn} C_{\sigma P} C_{\lambda n}\langle A\sigma\|1\lambda\rangle_{\alpha\beta\alpha\beta} + \\ &\sum_{\sigma\lambda}\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn} C_{\sigma n} C_{\lambda P}\langle A\sigma\|1\lambda\rangle_{\alpha\beta\alpha\beta} \qquad \text{(B.43)}\end{aligned}$$

$$\begin{aligned}\sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda}\langle A\sigma\|1\lambda\rangle &= \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle AP\|1m\rangle_{\alpha\alpha\alpha\alpha} + \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle Am\|1P\rangle_{\alpha\alpha\alpha\alpha} + \\ &\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle AP\|1n\rangle_{\alpha\beta\alpha\beta} + \sum_{n}^{\beta}\sum_{Pn} U^{\chi}_{Pn}\langle An\|1P\rangle_{\alpha\beta\alpha\beta} \qquad \text{(B.44)}\end{aligned}$$

Substituting (B.44) and (B.41) back into (B.39) we arrive at:

$$\begin{aligned}{}^{\alpha}f^{\chi}_{A1} &= h^{\chi}_{A1} + \sum_{m}^{\alpha}\langle Am\|1m\rangle^{\chi}_{\alpha\alpha\alpha\alpha} + \sum_{n}^{\beta}\langle An\|1n\rangle^{\chi}_{\alpha\beta\alpha\beta} + \\ &\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle AP\|1m\rangle_{\alpha\alpha\alpha\alpha} + \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle Am\|1P\rangle_{\alpha\alpha\alpha\alpha} + \\ &\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle AP\|1n\rangle_{\alpha\beta\alpha\beta} + \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle An\|1P\rangle_{\alpha\beta\alpha\beta} \qquad \text{(B.45)}\end{aligned}$$

Now let's look at the other two pieces.

$$\frac{\partial\,{}^{\alpha}f_{A1}}{\partial\chi} = 0 = \sum_{\mu\nu}\left[\frac{\partial C_{\mu A}}{\partial\chi}\,{}^{\alpha}f_{\mu\nu}C_{\nu 1} + {}^{\alpha}f^{\chi}_{A1} + C_{\mu A}\,{}^{\alpha}f_{\mu\nu}\frac{\partial C_{\nu 1}}{\partial\chi}\right] \qquad \text{(B.46)}$$

Using equation (B.7),

$$\frac{\partial\, {}^{\alpha}f_{A1}}{\partial\chi} = 0 \;=\; \sum_{\mu\nu}\left[\sum_{P} U^{\chi}_{PA} C_{\mu P}\, {}^{\alpha}f_{\mu\nu} C_{\nu 1} + {}^{\alpha}f^{\chi}_{A1} + \sum_{P} U^{\chi}_{P1} C_{\nu P}\, {}^{\alpha}f_{\mu\nu} C_{\mu A}\right] \quad \text{(B.47)}$$

$$0 \;=\; \sum_{P} U^{\chi}_{PA}\, {}^{\alpha}f_{P1} + {}^{\alpha}f^{\chi}_{A1} + \sum_{P} U^{\chi}_{P1}\, {}^{\alpha}f_{AP} \quad \text{(B.48)}$$

Let's expand the first and third terms of the last equation.

$$\sum_{P} U^{\chi}_{PA}\, {}^{\alpha}f_{P1} \;=\; \sum_{J} U^{\chi}_{JA}\, {}^{\alpha}f_{J1} + \sum_{2} U^{\chi}_{2A}\, {}^{\alpha}f_{21} + \sum_{B} U^{\chi}_{BA}\, {}^{\alpha}f_{B1} \quad \text{(B.49)}$$

$$\sum_{P} U^{\chi}_{P1}\, {}^{\alpha}f_{AP} \;=\; \sum_{J} U^{\chi}_{J1}\, {}^{\alpha}f_{AJ} + \sum_{2} U^{\chi}_{21}\, {}^{\alpha}f_{A2} + \sum_{B} U^{\chi}_{B1}\, {}^{\alpha}f_{AB} \quad \text{(B.50)}$$

The last term of equation (B.49) and the second term of equation (B.50) disappear because of the second ROHF condition. Substituting (B.50), (B.49), and (B.48) into (B.45) gives the full second equation needed:

$$\begin{aligned}
&\sum_{J} U^{\chi}_{JA}\, {}^{\alpha}f_{J1} + \sum_{2} U^{\chi}_{2A}\, {}^{\alpha}f_{21} + \sum_{J} U^{\chi}_{J1}\, {}^{\alpha}f_{AJ} + \sum_{B} U^{\chi}_{B1}\, {}^{\alpha}f_{AB} + \\
&\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle AP\|1m\rangle_{\alpha\alpha\alpha\alpha} + \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle Am\|1P\rangle_{\alpha\alpha\alpha\alpha} + \\
&\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle AP\|1n\rangle_{\alpha\beta\alpha\beta} + \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle An\|1P\rangle_{\alpha\beta\alpha\beta} \\
= \;& -\left[h^{\chi}_{A1} + \sum_{m}^{\alpha}\langle Am\|1m\rangle^{\chi}_{\alpha\alpha\alpha\alpha} + \sum_{n}^{\beta}\langle An\|1n\rangle^{\chi}_{\alpha\beta\alpha\beta}\right] \qquad \text{(B.51)}
\end{aligned}$$

Let's now derive the necessary expression from the third ROHF condition (Eqn. (B.3)).

$${}^{\beta}f_{1I} = \sum_{\mu\nu} C_{\mu 1}\, {}^{\beta}f_{\mu\nu} C_{\nu I} \quad \text{(B.52)}$$

$$\frac{\partial\, {}^{\beta}f_{1I}}{\partial\chi} = 0 = \sum_{\mu\nu}\left[\frac{\partial C_{\mu 1}}{\partial\chi}\,{}^{\beta}f_{\mu\nu}C_{\nu 1} + c_{\mu 1}\frac{\partial\, {}^{\beta}f_{\mu\nu}}{\partial\chi}C_{\nu I} + C_{\mu 1}\,{}^{\beta}f_{\mu\nu}\frac{\partial C_{\nu I}}{\partial\chi}\right] \tag{B.53}$$

Using equation (B.7), the last equation becomes

$$0 = \sum_{\mu\nu}\left[\sum_{P} U^{\chi}_{P1}C_{\mu P}\,{}^{\beta}f_{\mu\nu}C_{\nu I} + {}^{\beta}f^{\chi}_{1I} + \sum_{P} U^{\chi}_{PI}C_{\nu P}\,{}^{\beta}f_{\mu\nu}C_{\mu 1}\right] \tag{B.54}$$

where

$${}^{\beta}f^{\chi}_{1I} = C_{\mu 1}\frac{\partial\, {}^{\beta}f_{\mu\nu}}{\partial\chi}C_{\nu I}$$

This leads to

$$0 = \sum_{P} U^{\chi}_{P1}\,{}^{\beta}f_{PI} + {}^{\beta}f^{\chi}_{1I} + \sum_{P} U^{\chi}_{PI}\,{}^{\beta}f_{1P} \tag{B.55}$$

Expanding the first and third terms of this equation,

$$\sum_{P} U^{\chi}_{P1}\,{}^{\beta}f_{PI} = \sum_{J} U^{\chi}_{J1}\,{}^{\beta}f_{JI} + \sum_{2} U^{\chi}_{21}\,{}^{\beta}f_{2I} + \sum_{B} U^{\chi}_{B1}\,{}^{\beta}f_{BI} \tag{B.56}$$

$$\sum_{P} U^{\chi}_{PI}\,{}^{\beta}f_{1P} = \sum_{J} U^{\chi}_{JI}\,{}^{\beta}f_{1J} + \sum_{2} U^{\chi}_{2I}\,{}^{\beta}f_{12} + \sum_{B} U^{\chi}_{BI}\,{}^{\beta}f_{1B} \tag{B.57}$$

Due to the third ROHF condition (Eqn. (B.3)), the second term of (B.56) and the first term of (B.57) disappear. This yields

$$\sum_{P} U^{\chi}_{P1}\,{}^{\beta}f_{PI} = \sum_{J} U^{\chi}_{J1}\,{}^{\beta}f_{JI} + \sum_{B} U^{\chi}_{B1}\,{}^{\beta}f_{BI} \tag{B.58}$$

$$\sum_{P} U^{\chi}_{PI}\,{}^{\beta}f_{1P} = \sum_{2} U^{\chi}_{2I}\,{}^{\beta}f_{12} + \sum_{B} U^{\chi}_{BI}\,{}^{\beta}f_{1B} \tag{B.59}$$

(B.60)

Now let us deal with ${}^{\beta}f^{\chi}_{1I}$.

$$ {}^{\beta}f_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma\lambda} D_{\sigma\lambda}\langle\mu\sigma\|\nu\lambda\rangle \tag{B.61} $$

$$ \frac{\partial\, {}^{\beta}f_{\mu\nu}}{\partial\chi} = \frac{\partial h_{\mu\nu}}{\partial\chi} + sum_{\sigma\lambda}\frac{\partial D_{\sigma\lambda}}{\partial\chi}\langle\mu\sigma\|\nu\lambda\rangle + \sum_{\sigma\lambda} D_{\sigma\lambda}\frac{\partial\langle\mu\sigma\|\nu\lambda\rangle}{\partial\chi} \tag{B.62} $$

$$ {}^{\beta}f^{\chi}_{\mu\nu} = h^{\chi}_{\mu\nu} + \sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda}\langle\mu\sigma\|\nu\lambda\rangle + \sum_{\sigma\lambda} D_{\sigma\lambda}\langle\mu\sigma\|\nu\lambda\rangle^{\chi} \tag{B.63} $$

$$ {}^{\beta}f^{\chi}_{1I} = \sum_{\mu\nu}\left[C_{\mu 1}h^{\chi}_{\mu\nu}C_{\nu I} + \sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda}\langle\mu\sigma\|\nu\lambda\rangle C_{\mu 1}C_{\nu I} + \sum_{\sigma\lambda} D_{\sigma\lambda}\langle\mu\sigma\|\nu\lambda\rangle^{\chi} C_{\mu 1}C_{\nu I}\right] \tag{B.64} $$

$$ {}^{\beta}f^{\chi}_{1I} = h^{\chi}_{1I} + \sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda}\langle 1\sigma\|I\lambda\rangle + \sum_{\sigma\lambda} D_{\sigma\lambda}\langle 1\sigma\|I\lambda\rangle^{\chi} \tag{B.65} $$

$$ \begin{aligned} \sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda}\langle 1\sigma\|I\lambda\rangle \;=\; & \sum_{\sigma\lambda}\sum_{n}^{\beta}\frac{\partial C_{\sigma n}}{\partial\chi}C_{\lambda n}\langle 1\sigma\|I\lambda\rangle_{\beta\beta\beta\beta} + \sum_{\sigma\lambda}\sum_{n}^{\beta} C_{\sigma n}\frac{\partial C_{\lambda n}}{\partial\chi}\langle 1\sigma\|I\lambda\rangle_{\beta\beta\beta\beta} + \\ & \sum_{\sigma\lambda}\sum_{m}^{\alpha}\frac{\partial C_{\sigma m}}{\partial\chi}C_{\lambda m}\langle 1\sigma\|I\lambda\rangle_{\beta\alpha\beta\alpha} + \sum_{\sigma\lambda}\sum_{m}^{\alpha} C_{\sigma m}\frac{\partial C_{\lambda m}}{\partial\chi}\langle 1\sigma\|I\lambda\rangle_{\beta\alpha\beta\alpha} \end{aligned} \tag{B.66} $$

$$ \begin{aligned} \sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda}\langle 1\sigma\|I\lambda\rangle \;=\; & \sum_{\sigma\lambda}\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}C_{\sigma P}C_{\lambda n}\langle 1\sigma\|I\lambda\rangle_{\beta\beta\beta\beta} + \\ & \sum_{\sigma\lambda}\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}C_{\sigma n}C_{\lambda P}\langle 1\sigma\|I\lambda\rangle_{\beta\beta\beta\beta} + \\ & \sum_{\sigma\lambda}\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}C_{\sigma P}C_{\lambda m}\langle 1\sigma\|I\lambda\rangle_{\beta\alpha\beta\alpha} + \end{aligned} $$

$$\sum_{\sigma\lambda}\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm} C_{\sigma m} C_{\lambda P} \langle 1\sigma \| I\lambda \rangle_{\beta\alpha\beta\alpha} \tag{B.67}$$

$$\begin{aligned}\sum_{\sigma\lambda} D^{\chi}_{\sigma\lambda} \langle 1\sigma \| I\lambda \rangle \;=\; & \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn} \langle 1P \| In \rangle_{\beta\beta\beta\beta} + \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn} \langle 1n \| IP \rangle_{\beta\beta\beta\beta} + \\ & \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm} \langle 1P \| Im \rangle_{\beta\alpha\beta\alpha} + \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm} \langle 1m \| IP \rangle_{\beta\alpha\beta\alpha}\end{aligned} \tag{B.68}$$

$$\sum_{\sigma\lambda} D_{\sigma\lambda} \langle 1\sigma \| I\lambda \rangle^{\chi} = \sum_{\sigma\lambda}\sum_{n}^{\beta} C_{\sigma n} C_{\lambda n} \langle 1\sigma \| I\lambda \rangle^{\chi}_{\beta\beta\beta\beta} + \sum_{\sigma\lambda}\sum_{m}^{\alpha} C_{\sigma m} C_{\lambda m} \langle 1\sigma \| I\lambda \rangle^{\chi}_{\beta\alpha\beta\alpha} \tag{B.69}$$

$$\sum_{\sigma\lambda} D_{\sigma\lambda} \langle 1\sigma \| I\lambda \rangle^{\chi} = \sum_{n}^{\beta} \langle 1n \| In \rangle^{\chi}_{\beta\beta\beta\beta} + \sum_{m}^{\alpha} \langle 1m \| Im \rangle^{\chi}_{\beta\alpha\beta\alpha} \tag{B.70}$$

Substituting (B.70) and (B.68) into (B.65) yields

$$\begin{aligned}{}^{\beta}f^{\chi}_{1I} \;=\; & h^{\chi}_{1I} + \sum_{n}^{\beta} \langle 1n \| In \rangle^{\chi}_{\beta\beta\beta\beta} + \sum_{m}^{\alpha} \langle 1m \| Im \rangle^{\chi}_{\beta\alpha\beta\alpha} + \\ & \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn} \langle 1P \| In \rangle_{\beta\beta\beta\beta} + \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn} \langle 1n \| IP \rangle_{\beta\beta\beta\beta} + \\ & \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm} \langle 1P \| Im \rangle_{\beta\alpha\beta\alpha} + \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm} \langle 1m \| IP \rangle_{\beta\alpha\beta\alpha}\end{aligned} \tag{B.71}$$

The third overall equation can now be written using (B.71), (B.60), and (B.59) in (B.55):

$$\sum_{J} U^{\chi}_{J1}\, {}^{\beta}f_{JI} + \sum_{B} U^{\chi}_{B1}\, {}^{\beta}f_{BI} + \sum_{2} U^{\chi}_{2I}\, {}^{\beta}f_{12} + \sum_{B} U^{\chi}_{BI}\, {}^{\beta}f_{1B} +$$

$$\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle 1P\|In\rangle_{\beta\beta\beta\beta} + \sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle 1n\|IP\rangle_{\beta\beta\beta\beta} +$$

$$\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle 1P\|Im\rangle_{\beta\alpha\beta\alpha} + \sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle 1m\|IP\rangle_{\beta\alpha\beta\alpha}$$

$$= -\left[h^{\chi}_{1I} + \sum_{n}^{\beta}\langle 1n\|In\rangle^{\chi}_{\beta\beta\beta\beta} + \sum_{m}^{\alpha}\langle 1m\|Im\rangle^{\chi}_{\beta\alpha\beta\alpha}\right] \tag{B.72}$$

The other two overall equations are (B.32) and (B.51).

There remain three classes of U^{χ}'s to deal with. Of these, the only ones we wish to deal with are those which are indicated with asterisks (*):

$$\begin{Bmatrix} {}^{*}U_{AI} \\ U_{IA} \end{Bmatrix} \qquad \begin{Bmatrix} {}^{*}U_{1I} \\ U_{I1} \end{Bmatrix} \qquad \begin{Bmatrix} {}^{*}U_{A1} \\ U_{1A} \end{Bmatrix}$$

The U^{χ}'s in each class are related by the expression:

$$U^{\chi}_{pq} + U^{\chi}_{qp} = -S^{\chi}_{pq} \tag{B.73}$$

Using this relation, the left hand side (LHS) of equation B.72 becomes

$$\sum_{J} U^{\chi}_{J1}\,{}^{\beta}f_{JI} = \sum_{J}(-S^{\chi}_{1J} - U^{\chi}_{1J})\,{}^{\beta}f_{JI} \tag{B.74}$$

The lead term of the last equation is known and can be moved to the right hand side (RHS) of (B.72).

We can now break down the $\sum_{P}$ for the two-electron pieces on the LHS of (B.72). Since we have included a spin orbital index on each U^{χ}, this determines the spin on P (it must match or $U^{\chi} = 0$). Since we need only deal with spin orbitals for P, we can break each $\sum_{P}$ to be over occupied and virtual pieces. The four terms can therefore be expanded as shown below:

$$\begin{aligned}
\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle 1P\|In\rangle_{\beta\beta\beta\beta} &= \sum_{n}^{\beta}\sum_{o}^{\beta} U^{\chi}_{on}\langle 1o\|In\rangle_{\beta\beta\beta\beta} + \sum_{n}^{\beta}\sum_{e} U^{\chi}_{en}\langle 1e\|In\rangle_{\beta\beta\beta\beta} \\
\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle 1n\|IP\rangle_{\beta\beta\beta\beta} &= \sum_{n}^{\beta}\sum_{o}^{\beta} U^{\chi}_{on}\langle 1n\|Io\rangle_{\beta\beta\beta\beta} + \sum_{n}^{\beta}\sum_{e} U^{\chi}_{en}\langle 1n\|Ie\rangle_{\beta\beta\beta\beta} \\
\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle 1P\|Im\rangle_{\beta\alpha\beta\alpha} &= \sum_{m}^{\alpha}\sum_{l}^{\alpha} U^{\chi}_{lm}\langle 1l\|Im\rangle_{\beta\alpha\beta\alpha} + \sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\langle 1f\|Im\rangle_{\beta\alpha\beta\alpha} \\
\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle 1m\|IP\rangle_{\beta\alpha\beta\alpha} &= \sum_{m}^{\alpha}\sum_{l}^{\alpha} U^{\chi}_{lm}\langle 1m\|Il\rangle_{\beta\alpha\beta\alpha} + \sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\langle 1m\|If\rangle_{\beta\alpha\beta\alpha}
\end{aligned} \tag{B.75}$$

Since several of the terms in the last equation are double sums which run over the same range (such as the first term), the labels are arbitrary and can be rearranged. Doing so yields

$$\begin{aligned}
&\sum_{n}^{\beta}\sum_{o}^{\beta}\left(U^{\chi}_{on} + U^{\chi}_{no}\right)\langle 1o\|In\rangle_{\beta\beta\beta\beta} + \sum_{n}^{\beta}\sum_{e} U^{\chi}_{en}\left(\langle 1e\|In\rangle_{\beta\beta\beta\beta} + \langle 1n\|Ie\rangle_{\beta\beta\beta\beta}\right) \\
&\sum_{m}^{\alpha}\sum_{l}^{\alpha}\left(U^{\chi}_{lm} + U^{\chi}_{ml}\right)\langle 1l\|Im\rangle_{\beta\alpha\beta\alpha} + \sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\left(\langle 1f\|Im\rangle_{\beta\alpha\beta\alpha} + \langle 1m\|If\rangle_{\beta\alpha\beta\alpha}\right)
\end{aligned} \tag{B.76}$$

From (B.19) we can now express the last equation as

$$\begin{aligned}
&\sum_{n}^{\beta}\sum_{o}^{\beta}\left(-S^{\chi}_{on}\right)\langle 1o\|In\rangle_{\beta\beta\beta\beta} + \sum_{n}^{\beta}\sum_{e} U^{\chi}_{en}\left(\langle 1e\|In\rangle_{\beta\beta\beta\beta} + \langle 1n\|Ie\rangle_{\beta\beta\beta\beta}\right) + \\
&\sum_{m}^{\alpha}\sum_{l}^{\alpha}\left(-S^{\chi}_{lm}\right)\langle 1l\|Im\rangle_{\beta\alpha\beta\alpha} + \sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\left(\langle 1f\|Im\rangle_{\beta\alpha\beta\alpha} + \langle 1m\|If\rangle_{\beta\alpha\beta\alpha}\right)
\end{aligned} \tag{B.77}$$

Equation (B.72) can now be written as

$$\sum_J (-U^x)^{\beta} f_{JI} + \sum_B \left(U^x_{B1}{}^{\beta} f_{BI} + U^x_{BI}{}^{\beta} f_{1B} \right) + \sum_2 U^x_{2I}{}^{\beta} f_{12} +$$

$$\sum_n^{\beta} \sum_e U^x_{en} \left(\langle 1e \| In \rangle_{\beta\beta\beta\beta} + \langle 1n \| Ie \rangle_{\beta\beta\beta\beta} \right) +$$

$$\sum_m^{\alpha} \sum_f U^x_{fm} \left(\langle 1f \| Im \rangle_{\beta\alpha\beta\alpha} + \langle 1m \| If \rangle_{\beta\alpha\beta\alpha} \right)$$

$$= -\left[h^x_{1I} - \sum_J S^x_{1J}{}^{\beta} f_{JI} + \sum_n^{\beta} \langle 1n \| In \rangle^x_{\beta\beta\beta\beta} + \sum_m^{\alpha} \langle 1m \| Im \rangle^x_{\beta\alpha\beta\alpha} \right.$$

$$\left. - \sum_{no}^{\beta} S^x_{on} \langle 1o \| In \rangle_{\beta\beta\beta\beta} - \sum_{ml}^{\alpha} S^x_{lm} \langle 1l \| Im \rangle_{\beta\alpha\beta\alpha} \right] \qquad \text{(B.78)}$$

Now let's perform similar manipulations on equation (B.51). The first four terms of (B.51) are of the $U^x f$ type. Using (B.73), we can rewrite these terms in the following manner:

$$\begin{aligned}
\sum_J U^x_{JA}{}^{\alpha} f_{J1} &= \sum_J (-S^x_{AJ} - U^x_{AJ})^{\alpha} f_{J1} \\
\sum_2 U^x_{2A}{}^{\alpha} f_{21} &= \sum_2 (-S^x_{A2} - U^x_{A2})^{\alpha} f_{21} \\
\sum_J U^x_{J1}{}^{\alpha} f_{AJ} &= \sum_J (-S^x_{1J} - U^x_{1J})^{\alpha} f_{AJ} \\
\sum_B U^x_{B1}{}^{\alpha} f_{AB} & \qquad \text{(B.79)}
\end{aligned}$$

Rearranging terms yields

$$\sum_J (-S^x_{AJ}{}^{\alpha} f_{J1} - S^x_{1J}{}^{\alpha} f_{JA}) + \sum_2 (-S^x_{A2}{}^{\alpha} f_{21}) + \sum_J (-U^x_{AJ}{}^{\alpha} f_{J1} - U^x_{1J}{}^{\alpha} f_{JA}) +$$

$$\sum_{2}(-U^{\chi}_{A2}\,{}^{\alpha}f_{21}) + \sum_{B} U^{\chi}_{B1}\,{}^{\alpha}f_{AB} \tag{B.80}$$

The two-electron pieces of (B.51) can have the $\sum_{P}$ expanded into the spin-orbital basis which gives

$$\begin{aligned}
\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle AP\|1m\rangle_{\alpha\alpha\alpha\alpha} &= \sum_{m}^{\alpha}\sum_{l}^{\alpha} U^{\chi}_{lm}\langle Al\|1m\rangle_{\alpha\alpha\alpha\alpha} + \sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\langle Af\|1m\rangle_{\alpha\alpha\alpha\alpha} \\
\sum_{m}^{\alpha}\sum_{P} U^{\chi}_{Pm}\langle Am\|1P\rangle_{\alpha\alpha\alpha\alpha} &= \sum_{m}^{\alpha}\sum_{l}^{\alpha} U^{\chi}_{lm}\langle Am\|1l\rangle_{\alpha\alpha\alpha\alpha} + \sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\langle Am\|1f\rangle_{\alpha\alpha\alpha\alpha} \\
\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle AP\|1n\rangle_{\alpha\beta\alpha\beta} &= \sum_{n}^{\beta}\sum_{o}^{\beta} U^{\chi}_{on}\langle Ao\|1n\rangle_{\alpha\beta\alpha\beta} + \sum_{n}^{\beta}\sum_{e} U^{\chi}_{en}\langle Ae\|1n\rangle_{\alpha\beta\alpha\beta} \\
\sum_{n}^{\beta}\sum_{P} U^{\chi}_{Pn}\langle An\|1P\rangle_{\alpha\beta\alpha\beta} &= \sum_{n}^{\beta}\sum_{o}^{\beta} U^{\chi}_{on}\langle An\|1o\rangle_{\alpha\beta\alpha\beta} + \sum_{n}^{\beta}\sum_{e} U^{\chi}_{en}\langle An\|1e\rangle_{\alpha\beta\alpha\beta}
\end{aligned} \tag{B.81}$$

Using the same logic in going from (B.75) to (B.76), the last equation becomes

$$\begin{aligned}
&\sum_{m}^{\alpha}\sum_{l}^{\alpha}(U^{\chi}_{lm} + U^{\chi}_{ml})\,\langle Al\|1m\rangle_{\alpha\alpha\alpha\alpha} + \sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\,(\langle Af\|1m\rangle_{\alpha\alpha\alpha\alpha} + \langle Am\|1f\rangle_{\alpha\alpha\alpha\alpha}) + \\
&\sum_{n}^{\beta}\sum_{o}^{\beta}(U^{\chi}_{on} + U^{\chi}_{no})\,\langle Ao\|1n\rangle_{\alpha\beta\alpha\beta} + \sum_{n}^{\beta}\sum_{e} U^{\chi}_{en}\,(\langle Ae\|1n\rangle_{\alpha\beta\alpha\beta} + \langle An\|1e\rangle_{\alpha\beta\alpha\beta})
\end{aligned} \tag{B.82}$$

From (B.19) we can now express (B.82) as

$$\begin{aligned}
&\sum_{m}^{\alpha}\sum_{l}^{\alpha}(-S^{\chi}_{lm})\,\langle Al\|1m\rangle_{\alpha\alpha\alpha\alpha} + \sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\,(\langle Af\|1m\rangle_{\alpha\alpha\alpha\alpha} + \langle Am\|1f\rangle_{\alpha\alpha\alpha\alpha}) + \\
&\sum_{n}^{\beta}\sum_{o}^{\beta}(-S^{\chi}_{on})\,\langle Ao\|1n\rangle_{\alpha\beta\alpha\beta} + \sum_{n}^{\beta}\sum_{e} U^{\chi}_{en}\,(\langle Ae\|1n\rangle_{\alpha\beta\alpha\beta} + \langle An\|1e\rangle_{\alpha\beta\alpha\beta})
\end{aligned} \tag{B.83}$$

We can now write equation (B.51) as

$$\begin{aligned}
&\sum_J (-U^{\chi}_{AJ}{}^{\alpha}f_{J1} - U^{\chi}_{1J}{}^{\alpha}f_{JA}) + \sum_2 (-U^{\chi}_{A2}{}^{\alpha}f_{21}) + \sum_B U^{\chi}_{B1}{}^{\alpha}f_{AB} + \\
&\sum_m^{\alpha}\sum_f U^{\chi}_{fm}\left(\langle Af\|1m\rangle_{\alpha\alpha\alpha\alpha} + \langle Am\|1f\rangle_{\alpha\alpha\alpha\alpha}\right) + \\
&\sum_n^{\beta}\sum_e U^{\chi}_{en}\left(\langle Ae\|1n\rangle_{\alpha\beta\alpha\beta} + \langle An\|1e\rangle_{\alpha\beta\alpha\beta}\right) \\
= \quad &-\Bigg[h^{\chi}_{A1} - \sum_J (S^{\chi}_{AJ}{}^{\alpha}f_{J1} + S^{\chi}_{1J}{}^{\alpha}f_{JA}) - \sum_2 S^{\chi}_{A2}{}^{\alpha}f_{21} + \\
&\sum_m^{\alpha}\langle Am\|1m\rangle^{\chi}_{\alpha\alpha\alpha\alpha} + \sum_n^{\beta}\langle An\|1n\rangle^{\chi}_{\alpha\beta\alpha\beta} - \\
&\sum_{ml}^{\alpha} S^{\chi}_{lm}\langle Al\|1m\rangle_{\alpha\alpha\alpha\alpha} - \sum_{no}^{\beta} S^{\chi}_{on}\langle Ao\|1n\rangle_{\alpha\beta\alpha\beta}\Bigg]
\end{aligned} \tag{B.84}$$

We can now perform these same manipulations on (B.32). Using (B.73) where appropriate, the $U^{\chi}f$ terms of (B.32) are

$$\begin{aligned}
\sum_J U^{\chi}_{JA}\left({}^{\alpha}f_{JI} + {}^{\beta}f_{JI}\right) &= \sum_J (-S^{\chi}_{AJ} - U^{\chi}_{AJ})({}^{\alpha}f_{JI} + {}^{\alpha}f_{JI}) \\
\sum_1 \left(U^{\chi}_{1A}{}^{\alpha}f_{1I} + U^{\chi}_{1I}{}^{\beta}f_{A1}\right) &= \sum_1 \left(-S^{\chi}_{A1}{}^{\alpha}f_{1I} - U^{\chi}_{A1}{}^{\alpha}f_{1I} + U^{\chi}_{1I}{}^{\beta}f_{A1}\right) \\
\sum_B U^{\chi}_{BI}\left({}^{\alpha}f_{AB} + {}^{\beta}f_{AB}\right)
\end{aligned} \tag{B.85}$$

After rearranging terms we get

$$\begin{aligned}
&\sum_J (-S^{\chi}_{AJ})\left({}^{\alpha}f_{JI} + {}^{\beta}f_{JI}\right) + \sum 1\,(-S^{\chi}_{A1})\,{}^{\alpha}f_{1I} + \sum_1 \left(-U^{\chi}_{A1}{}^{\alpha}f_{1I} + U^{\chi}_{1I}{}^{\beta}f_{A1}\right) + \\
&\sum_B U^{\chi}_{BI}\left({}^{\alpha}f_{AB} + {}^{\beta}f_{AB}\right) + \sum_J (-U^{\chi}_{AJ})\left({}^{\alpha}f_{JI} + {}^{\beta}f_{JI}\right)
\end{aligned} \tag{B.86}$$

Using the expansion of $\sum_P$ into a spin-orbital basis, the two-electron pieces of (B.32) become

$$\begin{aligned}
\sum_m^{\alpha}\sum_P U^{\chi}_{Pm}\langle AP\|Im\rangle_{\alpha\alpha\alpha\alpha} &= \sum_m^{\alpha}\sum_l^{\alpha} U^{\chi}_{lm}\langle Al\|Im\rangle_{\alpha\alpha\alpha\alpha} + \sum_m^{\alpha}\sum_f U^{\chi}_{fm}\langle Af\|Im\rangle_{\alpha\alpha\alpha\alpha} \\
\sum_m^{\alpha}\sum_P U^{\chi}_{Pm}\langle Am\|IP\rangle_{\alpha\alpha\alpha\alpha} &= \sum_m^{\alpha}\sum_l^{\alpha} U^{\chi}_{lm}\langle Am\|Il\rangle_{\alpha\alpha\alpha\alpha} + \sum_m^{\alpha}\sum_f U^{\chi}_{fm}\langle Am\|If\rangle_{\alpha\alpha\alpha\alpha} \\
\sum_n^{\beta}\sum_P U^{\chi}_{Pn}\langle AP\|In\rangle_{\alpha\beta\alpha\beta} &= \sum_n^{\beta}\sum_o^{\beta} U^{\chi}_{on}\langle Ao\|In\rangle_{\alpha\beta\alpha\beta} + \sum_n^{\beta}\sum_e U^{\chi}_{en}\langle Ae\|In\rangle_{\alpha\beta\alpha\beta} \\
\sum_n^{\beta}\sum_P U^{\chi}_{Pn}\langle An\|IP\rangle_{\alpha\beta\alpha\beta} &= \sum_n^{\beta}\sum_o^{\beta} U^{\chi}_{on}\langle An\|Io\rangle_{\alpha\beta\alpha\beta} + \sum_n^{\beta}\sum_e U^{\chi}_{en}\langle An\|Ie\rangle_{\alpha\beta\alpha\beta} \\
\sum_n^{\beta}\sum_P U^{\chi}_{Pn}\langle AP\|In\rangle_{\beta\beta\beta\beta} &= \sum_n^{\beta}\sum_o^{\beta} U^{\chi}_{on}\langle Ao\|In\rangle_{\beta\beta\beta\beta} + \sum_n^{\beta}\sum_e U^{\chi}_{en}\langle Ae\|In\rangle_{\beta\beta\beta\beta} \\
\sum_n^{\beta}\sum_P U^{\chi}_{Pn}\langle An\|IP\rangle_{\beta\beta\beta\beta} &= \sum_n^{\beta}\sum_o^{\beta} U^{\chi}_{on}\langle An\|Io\rangle_{\beta\beta\beta\beta} + \sum_n^{\beta}\sum_e U^{\chi}_{en}\langle An\|Ie\rangle_{\beta\beta\beta\beta} \\
\sum_m^{\alpha}\sum_P U^{\chi}_{Pm}\langle AP\|Im\rangle_{\beta\alpha\beta\alpha} &= \sum_m^{\alpha}\sum_l^{\alpha} U^{\chi}_{lm}\langle Al\|Im\rangle_{\beta\alpha\beta\alpha} + \sum_m^{\alpha}\sum_f U^{\chi}_{fm}\langle Af\|Im\rangle_{\beta\alpha\beta\alpha} \\
\sum_m^{\alpha}\sum_P U^{\chi}_{Pm}\langle Am\|IP\rangle_{\beta\alpha\beta\alpha} &= \sum_m^{\alpha}\sum_l^{\alpha} U^{\chi}_{lm}\langle Am\|Il\rangle_{\beta\alpha\beta\alpha} + \sum_m^{\alpha}\sum_f U^{\chi}_{fm}\langle Am\|If\rangle_{\beta\alpha\beta\alpha}
\end{aligned} \tag{B.87}$$

Using the same logic in going from (B.75) to (B.76), the last equation becomes

$$\sum_m^{\alpha}\sum_l^{\alpha}\left(U^{\chi}_{lm}+U^{\chi}_{ml}\right)\langle Al\|Im\rangle_{\alpha\alpha\alpha\alpha} + \sum_m^{\alpha}\sum_f U^{\chi}_{fm}\left(\langle Af\|Im\rangle_{\alpha\alpha\alpha\alpha}+\langle Am\|If\rangle_{\alpha\alpha\alpha\alpha}\right) +$$

$$\sum_n^{\beta}\sum_o^{\beta}\left(U^{\chi}_{on}+U^{\chi}_{on}\right)\langle Ao\|In\rangle_{\alpha\beta\alpha\beta} + \sum_n^{\beta}\sum_e U^{\chi}_{en}\left(\langle Ae\|In\rangle_{\alpha\beta\alpha\beta}+\langle An\|Ie\rangle_{\alpha\beta\alpha\beta}\right) +$$

$$\sum_{n}^{\beta}\sum_{o}^{\beta}(U^{\chi}_{on}+U^{\chi}_{on})\,\langle Ao\|In\rangle_{\beta\beta\beta\beta}+\sum_{n}^{\beta}\sum_{e}U^{\chi}_{en}\,(\langle Ae\|In\rangle_{\beta\beta\beta\beta}+\langle An\|Ie\rangle_{\beta\beta\beta\beta})+$$

$$\sum_{m}^{\alpha}\sum_{l}^{\alpha}(U^{\chi}_{lm}+U^{\chi}_{ml})\,\langle Al\|Im\rangle_{\beta\alpha\beta\alpha}+\sum_{m}^{\alpha}\sum_{f}U^{\chi}_{fm}\,(\langle Af\|Im\rangle_{\beta\alpha\beta\alpha}+\langle Am\|If\rangle_{\beta\alpha\beta\alpha})$$

(B.88)

Using (B.19) and condensing summations, the previous equation becomes

$$\sum_{ml}^{\alpha}(-S^{\chi}_{lm})\,(\langle Al\|Im\rangle_{\alpha\alpha\alpha\alpha}+\langle Al\|Im\rangle_{\beta\alpha\beta\alpha})+\sum_{no}^{\beta}(-S^{\chi}_{on})\,(\langle Ao\|In\rangle_{\alpha\beta\alpha\beta}+$$

$$\langle Ao\|In\rangle_{\beta\beta\beta\beta})+$$

$$\sum_{m}^{\alpha}\sum_{f}U^{\chi}_{fm}\,(\langle Af\|Im\rangle_{\alpha\alpha\alpha\alpha}+\langle Af\|Im\rangle_{\beta\alpha\beta\alpha}+\langle Am\|If\rangle_{\alpha\alpha\alpha\alpha}+\langle Am\|If\rangle_{\beta\alpha\beta\alpha})+$$

$$\sum_{n}^{\beta}\sum_{e}U^{\chi}_{en}\,(\langle Ae\|In\rangle_{\alpha\beta\alpha\beta}+\langle Ae\|In\rangle_{\beta\beta\beta\beta}+\langle An\|Ie\rangle_{\alpha\beta\alpha\beta}+\langle An\|Ie\rangle_{\beta\beta\beta\beta})$$

(B.89)

We can now write (B.32) as

$$\sum_{J}(-U^{\chi}_{AJ})\left({}^{\alpha}f_{JI}+{}^{\beta}f_{JI}\right)+\sum_{1}\left(-U^{\chi}_{A1}\,{}^{\alpha}f_{1I}+U^{\chi}_{1I}\,{}^{\beta}f_{A1}\right)+\sum_{B}U^{\chi}_{BI}\left({}^{\alpha}f_{AB}+{}^{\beta}f_{AB}\right)+$$

$$\sum_{m}^{\alpha}\sum_{f}U^{\chi}_{fm}\,(\langle Af\|Im\rangle_{\alpha\alpha\alpha\alpha}+\langle Af\|Im\rangle_{\beta\alpha\beta\alpha}+\langle Am\|If\rangle_{\alpha\alpha\alpha\alpha}+\langle Am\|If\rangle_{\beta\alpha\beta\alpha})+$$

$$\sum_{n}^{\beta}\sum_{e}U^{\chi}_{en}\,(\langle Ae\|In\rangle_{\alpha\beta\alpha\beta}+\langle Ae\|In\rangle_{\beta\beta\beta\beta}+\langle An\|Ie\rangle_{\alpha\beta\alpha\beta}+\langle An\|Ie\rangle_{\beta\beta\beta\beta})$$

$$=\;-\Big[h^{\chi}_{AI}+h^{\chi}_{AI}-\sum_{J}S^{\chi}_{AJ}\left({}^{\alpha}f_{JI}+{}^{\beta}f_{JI}\right)-\sum_{1}S^{\chi}_{A1}\,{}^{\alpha}f_{1I}+\sum_{m}^{\alpha}\langle Am\|Im\rangle^{\chi}_{\alpha\alpha\alpha\alpha}+$$

$$\sum_{n}^{\beta}\langle An\|In\rangle^{\chi}_{\alpha\beta\alpha\beta}+\sum_{n}^{\beta}\langle An\|In\rangle^{\chi}_{\beta\beta\beta\beta}+\sum_{m}^{\alpha}\langle Am\|Im\rangle^{\chi}_{\beta\alpha\beta\alpha}$$

$$-\sum_{ml}^{\alpha} S^{\chi}_{lm}\left(\langle Al\|Im\rangle_{\alpha\alpha\alpha\alpha}+\langle Al\|Im\rangle_{\beta\alpha\beta\alpha}\right)$$

$$-\sum_{no}^{\beta} S^{\chi}_{on}\left(\langle Ao\|In\rangle_{\alpha\beta\alpha\beta}+\langle Ao\|In\rangle_{\beta\beta\beta\beta}\right)\Bigg] \tag{B.90}$$

Our current working equations are (B.90), (B.84), and (B.78). We need to convert the remaining $U^{\chi}f$ terms of these equations to the spin-orbital basis. If we examine these terms from equation (B.90), we see that they are

$$\sum_{J}(-U^{\chi}_{AJ})\left({}^{\alpha}f_{JI}+{}^{\beta}f_{JI}\right)+\sum_{1}\left(-U^{\chi}_{A1}{}^{\alpha}f_{1I}+U^{\chi}_{1I}{}^{\beta}f_{A1}\right)+\sum_{B}U^{\chi}_{BI}\left({}^{\alpha}f_{AB}+{}^{\beta}f_{AB}\right) \tag{B.91}$$

Recognizing that the singly occupied space is "occupied" for α spin and "virtual" for β spin, the terms in the last equation can be rearrange to

$$\sum_{m}^{\alpha}(-U^{\chi}_{Am})\,{}^{\alpha}f_{mI}+\sum_{n}^{\beta}(-U^{\chi}_{An})\,{}^{\beta}f_{nI}+\sum_{f}U^{\chi}_{fI}{}^{\alpha}f_{Af}+\sum_{e}U^{\chi}_{eI}{}^{\beta}f_{Ae} \tag{B.92}$$

It is important to note that the first part of the second term of (B.91) is now part of the first term in (B.92). This is because the $A1$ term is a virtual-occupied piece for α spin and needs to be combined with the doubly occupied space of the first term of (B.91) to span the complete α spin subspace. Similarly, the second part of the second term of (B.91) is now contained in the last term of (B.92), since it is required to span the complete virtual β spin subspace.

We can now use these terms to begin to derive an expression for the CPHF equation. We want to associate terms based on the spin cases of AI and the other indices (fm or en).

Case 1: $AI = \alpha\alpha$, $fm = \alpha\alpha$

$$\text{LHS: } \sum_{m}^{\alpha}(-U^{\chi}_{Am})\,{}^{\alpha}f_{mI} + \sum_{f} U^{\chi}_{fI}\,{}^{\alpha}f_{Af} + \sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\left(\langle Af\|Im\rangle_{\alpha\alpha\alpha\alpha} + \langle Am\|If\rangle_{\alpha\alpha\alpha\alpha}\right)$$

$$\text{RHS: } -\left[-\sum_{m}^{\alpha} S^{\chi}_{Am}\,{}^{\alpha}f_{mI} + \sum_{m}^{\alpha}\langle Am\|Im\rangle^{\chi}_{\alpha\alpha\alpha\alpha} - \sum_{ml}^{\alpha} S^{\chi}_{lm}\langle Al\|Im\rangle_{\alpha\alpha\alpha\alpha} + h^{\chi}_{AI}\right]$$

Case 2: $AI = \alpha\alpha$, $en = \beta\beta$

$$\text{LHS: } \sum_{n}^{\beta}\sum_{e} U^{\chi}_{en}\left(\langle Ae\|In\rangle_{\alpha\beta\alpha\beta} + \langle An\|Ie\rangle_{\alpha\beta\alpha\beta}\right)$$

$$\text{RHS: } -\left[\sum_{n}^{\beta}\langle An\|In\rangle^{\chi}_{\alpha\beta\alpha\beta} - \sum_{no}^{\beta} S^{\chi}_{on}\langle Ao\|In\rangle_{\alpha\beta\alpha\beta}\right]$$

Case 3: $AI = \beta\beta$, $fm = \alpha\alpha$

$$\text{LHS: } \sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\left(\langle Af\|Im\rangle_{\beta\alpha\beta\alpha} + \langle Am\|If\rangle_{\beta\alpha\beta\alpha}\right)$$

$$\text{RHS: } -\left[\sum_{m}^{\alpha}\langle Am\|Im\rangle^{\chi}_{\beta\alpha\beta\alpha} - \sum_{ml}^{\alpha} S^{\chi}_{lm}\langle Al\|Im\rangle_{\beta\alpha\beta\alpha}\right]$$

Case 4: $AI = \beta\beta$, $en = \beta\beta$

$$\text{LHS: } \sum_{n}^{\beta}(-U^{\chi}_{An})\,{}^{\beta}f_{nI} + \sum_{e} u^{\chi}_{eI}\,{}^{\beta}f_{Ae} + \sum_{n}^{\beta}\sum_{e} U^{\chi}_{en}\left(\langle Ae\|In\rangle_{\beta\beta\beta\beta} + \langle An\|Ie\rangle_{\beta\beta\beta\beta}\right)$$

$$\text{RHS: } -\left[-\sum_{n}^{\beta} S^{\chi}_{An}\,{}^{\beta}f_{nI} + \sum_{n}^{\beta}\langle An\|In\rangle^{\chi}_{\beta\beta\beta\beta} - \sum_{no}^{\beta} S^{\chi}_{on}\langle Ao\|In\rangle_{\beta\beta\beta\beta} + h^{\chi}_{AI}\right] \tag{B.93}$$

Examining equation (B.84), the $U^{\chi}f$ terms are

$$\sum_J (-U^{\chi}_{AJ}\,{}^{\alpha}f_{J1} - U^{\chi}_{1J}\,{}^{\alpha}f_{JA}) + \sum_2 (-U^{\chi}_{A2}\,{}^{\alpha}f_{21}) + \sum_B U^{\chi}_{B1}\,{}^{\alpha}f_{AB} \tag{B.94}$$

Using the same logic as used in going from (B.91) to (B.92), equation (B.94) becomes

$$\sum_m^{\alpha} (-U^{\chi}_{Am}\,{}^{\alpha}f_{m1}) + \sum_n^{\beta} (-U^{\chi}_{1n}\,{}^{\alpha}f_{nA}) + \sum_f U^{\chi}_{f1}\,{}^{\alpha}f_{Af} \tag{B.95}$$

where the second term of (B.94) has been put into the first term of (B.95). Let's look at the two possible spin cases for (B.84).

Case 1: $A1 = \alpha\alpha$, $fm = \alpha\alpha$

$$\text{LHS: } \sum_m^{\alpha} (-U^{\chi}_{Am}\,{}^{\alpha}f_{m1}) + \sum_f U^{\chi}_{f1}\,{}^{\alpha}f_{Af} + \sum_m^{\alpha}\sum_f U^{\chi}_{fm}\,(\langle Af\|1m\rangle_{\alpha\alpha\alpha\alpha} + \langle Am\|1f\rangle_{\alpha\alpha\alpha\alpha})$$

$$\text{RHS: } -\Bigg[-\sum_m^{\alpha} (S^{\chi}_{Am}\,{}^{\alpha}f_{m1} + S^{\chi}_{1m}\,{}^{\alpha}f_{mA}) + \sum_m^{\alpha}\langle Am\|1m\rangle^{\chi}_{\alpha\alpha\alpha\alpha} - \sum_{ml}^{\alpha} S^{\chi}_{lm}\langle Al\|1m\rangle_{\alpha\alpha\alpha\alpha} + h^{\chi}_{A1}\Bigg]$$

Case 2: $A1 = \alpha\alpha$, $en = \beta\beta$

$$\text{LHS: } \sum_n^{\beta}\sum_e U^{\chi}_{en}\,(\langle Ae\|1n\rangle_{\alpha\beta abeta\alpha} + \langle An\|1e\rangle_{\alpha\beta\alpha\beta}) + \sum_n^{\beta} (-U^{\chi}_{1n})\,{}^{\alpha}f_{nA}$$

$$\text{RHS: } -\left[\sum_n^{\beta}\langle An\|1n\rangle^{\chi}_{\alpha\beta\alpha\beta} - \sum_{no}^{\beta} S^{\chi}_{on}\langle Ao\|1n\rangle_{\alpha\beta\alpha\beta}\right]$$

(B.96)

Examining equation (B.78), the $U^{\chi}f$ terms are:

$$\sum_J (-U^{\chi}_{1J})^{\beta} f_{JI} + \sum_B \left(U^{\chi}_{B1}{}^{\beta} f_{BI} + U^{\chi}_{B\bar{I}}{}^{\beta} f_{1B} \right) + \sum_2 U^{\chi}_{2\bar{I}}{}^{\beta} f_{12} \tag{B.97}$$

Using the logic described earler, (B.97) can be rearranged to

$$\sum_n^{\beta} (-U^{\chi}_{1n})^{\beta} f_{nI} + \sum_e U^{\chi}_{e\bar{I}}{}^{\beta} f_{1e} + \sum_f U^{\chi}_{f1}{}^{\beta} f_{fI} \tag{B.98}$$

where the last term of (B.97) has been put in the second part of the last term of (B.98). Let's now look at the two possible spin cases.

Case 1: $1I = \beta\beta$, $fm = \alpha\alpha$

$$\text{LHS: } \sum_m^{\alpha} \sum_f U^{\chi}_{fm} \left(\langle 1f \| Im \rangle_{\beta\alpha\beta\alpha} + \langle 1m \| If \rangle_{\beta\alpha\beta\alpha} \right) + \sum_f U^{\chi}_{f1}{}^{\beta} f_{fI}$$

$$\text{RHS: } - \left[\sum_m^{\alpha} \langle 1m \| Im \rangle^{\chi}_{\beta\alpha\beta\alpha} - \sum_{ml}^{\alpha} S^{\chi}_{lm} \langle 1l \| Im \rangle_{\beta\alpha\beta\alpha} \right]$$

Case 2: $1I = \beta\beta$, $en = \beta\beta$

$$\text{LHS: } \sum_n^{\beta} (-U^{\chi}_{1n})^{\beta} f_{nI} + \sum_e U^{\chi}_{e\bar{I}}{}^{\beta} f_{1e} + \sum_n^{\beta} \sum_e U^{\chi}_{en} \left(\langle 1e \| In \rangle_{\beta\beta\beta\beta} + \langle 1n \| Ie \rangle_{\beta\beta\beta\beta} \right)$$

$$\text{RHS: } - \left[- \sum_n^{\beta} S^{\chi}_{1n}{}^{\beta} f_{nI} + \sum_n^{\beta} \langle 1n \| In \rangle^{\chi}_{\beta\beta\beta\beta} - \sum_{no}^{\beta} S^{\chi}_{on} \langle 1o \| In \rangle_{\beta\beta\beta\beta} + h^{\chi}_{1I} \right] \tag{B.99}$$

We now need to take the spin-orbital basis expressions for each of the ROHF conditions (each of the cases given by (B.93), (B.96), and (B.99)) and put them in the general CPHF form.

The general form of the CPHF equations are

$$\mathcal{A}_{\alpha\alpha\alpha\alpha}U^{\chi}_{\alpha\alpha} + \mathcal{A}_{\alpha\alpha\beta\beta}U^{\chi}_{\beta\beta} = \mathcal{B}_{\alpha\alpha} \tag{B.100}$$

$$\mathcal{A}_{\beta\beta\beta\beta}U^{\chi}_{\beta\beta} + \mathcal{A}_{\beta\beta\alpha\alpha}U^{\chi}_{\alpha\alpha} = \mathcal{B}_{\beta\beta} \tag{B.101}$$

Now let's factor (B.93) so it resembles equations (B.100) and (B.101). Using cases 1 and 2 of (B.93) we can construct a piece similar to (B.100).

$$\begin{aligned}
&\left[\sum_{m}^{\alpha}(-U^{\chi}_{Am}{}^{\alpha}f_{mI}) + \sum_{f} U^{\chi}_{fI}{}^{\alpha}f_{Af}\right] + \sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\left(\langle Af\|Im\rangle + \langle Am\|If\rangle\right) + \\
&\sum_{n}^{\beta}\sum_{e} U^{\chi}_{en}\left(\langle Ae\|In\rangle + \langle An\|Ie\rangle\right) \\
= \;& -h^{\chi}_{AI} + \sum_{m}^{\alpha} S^{\chi}_{Am}{}^{\alpha}f_{mI} - \sum_{m}^{\alpha}\langle Am\|Im\rangle^{\chi} + \sum_{ml}^{\alpha} S^{\chi}_{lm}\langle Al\|Im\rangle - \sum_{n}^{\beta}\langle An\|In\rangle^{\chi} + \\
&\sum_{no}^{\beta} S^{\chi}_{on}\langle Ao\|In\rangle
\end{aligned} \tag{B.102}$$

Using cases 3 and 4 of (B.93), we get a piece similar to (B.101).

$$\begin{aligned}
&\left[\sum_{n}^{\beta}\left(-U^{\chi}_{An}{}^{\beta}f_{nI}\right) + \sum_{e} U^{\chi}_{eI}{}^{\beta}f_{Ae}\right] + \sum_{n}^{\beta}\sum_{e} U^{\chi}_{en}\left(\langle Ae\|In\rangle + \langle An\|Ie\rangle\right) + \\
&\sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\left(\langle Af\|Im\rangle + \langle Am\|If\rangle\right) \\
= \;& -h^{\chi}_{AI} + \sum_{n}^{\beta} S^{\chi}_{An}{}^{\beta}f_{nI} - \sum_{n}^{\beta}\langle An\|In\rangle^{\chi} + \sum_{no}^{\beta} S^{\chi}_{on}\langle Ao\|In\rangle - \sum_{m}^{\alpha}\langle Am\|Im\rangle^{\chi} + \\
&\sum_{ml}^{\alpha} S^{\chi}_{lm}\langle Al\|Im\rangle
\end{aligned} \tag{B.103}$$

Factoring (B.96) in a similar fashion yields

$$\left[\sum_{m}^{\alpha}(-U^{\chi}_{Am}{}^{\alpha}f_{m1})+\sum_{f}U^{\chi}_{f1}{}^{\alpha}f_{Af}\right]+\sum_{m}^{\alpha}\sum_{f}U^{\chi}_{fm}\left(\langle Af\|1m\rangle+\langle Am\|1f\rangle\right)+$$

$$\sum_{n}^{\beta}\sum_{e}U^{\chi}_{en}\left(\langle Ae\|1n\rangle+\langle An\|1e\rangle\right)+\sum_{n}^{\beta}\left(-U^{\chi}_{1n}{}^{\alpha}f_{nA}\right)$$

$$= \quad -h^{\chi}_{A1}+\sum_{m}^{\alpha}S^{\chi}_{Am}{}^{\alpha}f_{m1}-\sum_{m}^{\alpha}\langle Am\|1m\rangle^{\chi}+\sum_{ml}^{\alpha}S^{\chi}_{lm}\langle Al\|1m\rangle-\sum_{n}^{\beta}\langle An\|1n\rangle^{\chi}+$$

$$\sum_{no}^{\beta}S^{\chi}_{on}\langle Ao\|1n\rangle \tag{B.104}$$

Factoring (B.99) in this way yields

$$\left[\sum_{n}^{\beta}\left(-U^{\chi}_{1n}{}^{\beta}f_{nI}\right)+\sum_{e}U^{\chi}_{eI}{}^{\beta}f_{1e}\right]+\sum_{n}^{\beta}\sum_{e}U^{\chi}_{en}\left(\langle 1e\|In\rangle+\langle 1n\|Ie\rangle\right)+$$

$$\sum_{m}^{\alpha}\sum_{f}U^{\chi}_{fm}\left(\langle 1f\|Im\rangle+\langle 1m\|If\rangle\right)+\sum_{f}U^{\chi}_{f1}{}^{\beta}f_{fI}$$

$$= \quad -h^{\chi}_{1I}+\sum_{n}^{\beta}S^{\chi}_{1n}{}^{\beta}f_{nI}-\sum_{n}^{\beta}\langle 1n\|In\rangle^{\chi}+\sum_{no}^{\beta}S^{\chi}_{on}\langle 1o\|In\rangle-\sum_{m}^{\alpha}\langle 1m\|Im\rangle^{\chi}+$$

$$\sum_{ml}^{\alpha}S^{\chi}_{lm}\langle 1l\|Im\rangle \tag{B.105}$$

In the programs, we can easily calculate the full α and β blocks. The separation of the 1-space from α and β in the proper fashion is needed, but not for calculating the values. Looking at the LHS only, we have the following α pieces from equations (B.102) and (B.104):

$$\left[\sum_{m}^{\alpha}(-U^{\chi}_{Am})^{\alpha}f_{mI}+\sum_{f}U^{\chi}_{fI}{}^{\alpha}f_{Af}\right]+\sum_{m}^{\alpha}\sum_{f}U^{\chi}_{fm}\left(\langle Af\|Im\rangle+\langle Am\|If\rangle\right)+$$

$$\left[\sum_{m}^{\alpha}(-U^{X}_{Am})\,{}^{\alpha}f_{m1}+\sum_{f}U^{X}_{f1}\,{}^{\alpha}f_{Af}\right]+\sum_{m}^{\alpha}\sum_{f}U^{X}_{fm}\left(\langle Af\|1m\rangle+\langle Am\|1m\rangle\right) \tag{B.106}$$

Combining both these terms to cover the full α space, we get

$$\left[\sum_{m}^{\alpha}(-U^{X}_{am})\,{}^{\alpha}f_{mi}+\sum_{f}U^{X}_{fi}\,{}^{\alpha}f_{af}\right]+\sum_{m}^{\alpha}\sum_{f}U^{X}_{fm}\left(\langle af\|im\rangle+\langle am\|if\rangle\right) \tag{B.107}$$

To get the proper form for the $\mathcal{A}$ matrix in the CPHF equations, we need to be able to factor the U^{X}'s from each term. Doing this to (B.107) yields

$$\left[\sum_{m}^{\alpha}\sum_{f}\left(-U^{X}_{fm}\right)\,{}^{\alpha}f_{mi}+\sum_{m}^{\alpha}\sum_{f}\delta_{im}U^{X}_{fm}\,{}^{\alpha}f_{af}\right]+\sum_{m}^{\alpha}\sum_{f}U^{X}_{fm}\left(\langle af\|im\rangle+\langle am\|if\rangle\right) \tag{B.108}$$

$$\sum_{m}^{\alpha}\sum_{f}\left[-\delta_{af}\,{}^{\alpha}f_{mi}+\delta_{im}\,{}^{\alpha}f_{af}+\langle af\|im\rangle+\langle am\|if\rangle\right]U^{X}_{fm} \tag{B.109}$$

The general $\mathcal{A}$ matrix element for this spin case is therefore

$$\mathcal{A}_{aifm}=-\delta_{af}\,{}^{\alpha}f_{af}+\delta_{im}\,{}^{\alpha}f_{af}+\langle af\|im\rangle+\langle am\|if\rangle \tag{B.110}$$

Let's now look at the case for the LHS for $\beta\beta\beta\beta$. This takes the β terms from equations (B.103) and (B.105):

$$\left[\sum_{n}^{\beta}(-U^{X}_{An})\,{}^{\beta}f_{nI}+\sum_{e}U^{X}_{eI}\,{}^{\beta}f_{Ae}\right]+\sum_{n}^{\beta}\sum_{e}U^{X}_{en}\left(\langle Ae\|In\rangle+\langle An\|Ie\rangle\right)+$$

$$\left[\sum_{n}^{\beta}(-U^{X}_{1n})\,{}^{\beta}f_{nI}+\sum_{e}U^{X}_{eI}\,{}^{\beta}f_{1e}\right]+\sum_{n}^{\beta}\sum_{e}U^{X}_{en}\left(\langle 1e\|In\rangle+\langle An\|1e\rangle\right) \tag{B.111}$$

Combining these pieces to cover the full β space gives

$$\left[\sum_{n}^{\beta}(-U^{\chi}_{\bar{a}\bar{n}})^{\beta}f_{\bar{n}\bar{\imath}}+\sum_{e}U^{\chi}_{\bar{e}\bar{\imath}}{}^{\beta}f_{\bar{a}\bar{e}}\right]+\sum_{n}^{\beta}\sum_{e}U^{\chi}_{\bar{e}\bar{n}}\left(\langle\bar{a}\bar{e}\|\bar{\imath}\bar{n}\rangle+\langle\bar{a}\bar{n}\|\bar{\imath}\bar{e}\rangle\right) \tag{B.112}$$

Once again, we need to factor U^{χ}'s out to yield the form for the CPHF $\mathcal{A}$ matrix

$$\left[\sum_{n}^{\beta}\sum_{e}\delta_{\bar{e}\bar{a}}\,(-U^{\chi}_{\bar{e}\bar{n}})^{\beta}f_{\bar{n}\bar{\imath}}+\sum_{n}^{\beta}\sum_{e}\delta_{\bar{\imath}\bar{n}}U^{\chi}_{\bar{e}\bar{n}}{}^{\beta}f_{\bar{a}\bar{e}}\right]+\sum_{n}^{\beta}\sum_{e}\left(\langle\bar{a}\bar{e}\|\bar{\imath}\bar{n}\rangle+\langle\bar{a}\bar{n}\|\bar{\imath}\bar{e}\rangle\right) \tag{B.113}$$

$$\sum_{n}^{\beta}\sum_{e}\left[-\delta_{\bar{e}\bar{a}}{}^{\beta}f_{\bar{n}\bar{\imath}}+\delta_{\bar{\imath}\bar{n}}{}^{\beta}f_{\bar{a}\bar{e}}+\langle\bar{a}\bar{e}\|\bar{\imath}\bar{n}\rangle+\langle\bar{a}\bar{n}\|\bar{\imath}\bar{e}\rangle\right]U^{\chi}_{\bar{e}\bar{n}} \tag{B.114}$$

The general $\mathcal{A}$ matrix element for this spin case is therefore

$$\mathcal{A}_{\bar{a}\bar{\imath}\bar{e}\bar{n}}=-\delta_{\bar{e}\bar{a}}{}^{\beta}f_{\bar{n}\bar{\imath}}+\delta_{\bar{\imath}\bar{n}}{}^{\beta}f_{\bar{a}\bar{e}}+\langle\bar{a}\bar{e}\|\bar{\imath}\bar{n}\rangle+\langle\bar{a}\bar{n}\|\bar{\imath}\bar{e}\rangle \tag{B.115}$$

We now need the cross terms, with respect to spin. The β parts of equations (B.102) and (B.104) for the LHS give us $\alpha\beta\alpha\beta$:

$$\sum_{n}^{\beta}\sum_{e}U^{\chi}_{en}\left(\langle Ae\|In\rangle+\langle An\|Ie\rangle\right)+\sum_{n}^{\beta}\sum_{e}U^{\chi}_{en}\left(\langle Ae\|In\rangle+\langle An\|Ie\rangle\right)$$
$$+\sum_{n}^{\beta}(-U^{\chi}_{1n})^{\alpha}f_{nA} \tag{B.116}$$

Combining these pieces gives us

$$\sum_{n}^{\beta}\sum_{e}U^{\chi}_{\bar{e}\bar{n}}\left(\langle a\bar{e}\|i\bar{n}\rangle+\langle a\bar{n}\|i\bar{e}\rangle\right)+\sum_{n}^{\beta}(-U^{\chi}_{1n})^{\alpha}f_{nA} \tag{B.117}$$

We need to deal with the last term of the previous equation. Since the first ROHF condition (equation (B.1)) is ${}^{\alpha}f_{AI} + {}^{\beta}f_{AI} = 0$, then ${}^{\alpha}f_{AI} = -{}^{\beta}f_{AI}$. Making this substitution gives

$$\sum_{n}^{\beta} \left(-U^{\chi}_{1n}\right) \left(-{}^{\beta}f_{nA}\right) \tag{B.118}$$

Continuing with the U^{χ} factorization gives

$$\sum_{n}^{\beta} \sum_{e} U^{\chi}_{\bar{e}n} \left(\langle a\bar{e} \| i\bar{n} \rangle + \langle a\bar{n} \| i\bar{e} \rangle \right) + \sum_{n}^{\beta} \sum_{e} \delta_{\bar{e}1} U^{\chi}_{\bar{e}\bar{n}} {}^{\beta}f_{\bar{n}\bar{a}} \tag{B.119}$$

Recognizing that 1 is occupied for α, the last equation becomes

$$\sum_{n}^{\beta} \sum_{e} U^{\chi}_{\bar{e}\bar{n}} \left(\langle a\bar{e} \| i\bar{n} \rangle + \langle a\bar{n} \| i\bar{e} \rangle \right) + \sum_{n}^{\beta} \sum_{e} \delta_{\bar{e}i} U^{\chi}_{\bar{e}\bar{n}} {}^{\beta}f_{\bar{n}\bar{e}} \tag{B.120}$$

$$\sum_{n}^{\beta} \sum_{e} \left[\langle a\bar{e} \| i\bar{n} \rangle + \langle a\bar{n} \| i\bar{e} \rangle + \delta_{\bar{e}i} {}^{\beta}f_{\bar{n}\bar{a}} \right] U^{\chi}_{\bar{e}\bar{n}} \tag{B.121}$$

The general $\mathcal{A}$ matrix element for this spin case is therefore

$$\mathcal{A}_{ai\bar{e}\bar{n}} = \langle a\bar{e} \| i\bar{n} \rangle + \langle a\bar{n} \| i\bar{e} \rangle + \delta_{\bar{e}i} {}^{\beta}f_{\bar{n}\bar{a}} \tag{B.122}$$

The last spin case comes from the α parts of equations (B.103) and (B.105):

$$\sum_{m}^{\alpha} \sum_{f} U^{\chi}_{fm} \left(\langle Af \| Im \rangle + \langle Am \| If \rangle \right) + \sum_{m}^{\alpha} \sum_{f} U^{\chi}_{fm} \left(\langle 1f \| Im \rangle + \langle 1m \| If \rangle \right)$$
$$+ \sum_{f} U^{\chi}_{f1} {}^{\beta}f_{fI} \tag{B.123}$$

Combining terms is this equation yields

$$\sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\left(\langle \bar{a}f\|\bar{\imath}m\rangle + \langle \bar{a}m\|\bar{\imath}f\rangle\right) + \sum_{f} U^{\chi}_{f1}{}^{\beta} f_{fI} \tag{B.124}$$

Continuing with the U^{χ} factorization gives

$$\sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\left(\langle \bar{a}f\|\bar{\imath}m\rangle + \langle \bar{a}m\|\bar{\imath}f\rangle\right) + \sum_{m}^{\alpha}\sum_{f} \delta_{m1} U^{\chi}_{fm}{}^{\beta} f_{fI} \tag{B.125}$$

Recognizing that 1 for β is unoccupied, the last equation becomes

$$\sum_{m}^{\alpha}\sum_{f} U^{\chi}_{fm}\left(\langle \bar{a}f\|\bar{\imath}m\rangle + \langle \bar{a}m\|\bar{\imath}f\rangle\right) + \sum_{m}^{\alpha}\sum_{f} \delta_{m\bar{a}} U^{\chi}_{fm}{}^{\beta} f_{f\bar{\imath}} \tag{B.126}$$

$$\sum_{m}^{\alpha}\sum_{f} \left[\langle \bar{a}f\|\bar{\imath}m\rangle + \langle \bar{a}m\|\bar{\imath}f\langle + \delta_{m\bar{a}}{}^{\beta} f_{f\bar{\imath}}\right] U^{\chi}_{fm} \tag{B.127}$$

This gives the general $\mathcal{A}$ matrix element for this spin case as

$$\mathcal{A}_{\bar{a}\bar{\imath}fm} = \langle \bar{a}f\|\bar{\imath}m\rangle + \langle \bar{a}m\|\bar{\imath}f\rangle + \delta_{m\bar{a}}{}^{\beta} f_{f\bar{\imath}} \tag{B.128}$$

The various $\mathcal{A}$ matrix elements are

$$\begin{aligned}
\mathcal{A}_{ai fm} &= \langle af\|im\rangle + \langle am\|if\rangle + \delta_{im}{}^{\alpha} f_{af} - \delta_{af}{}^{\alpha} f_{mi} \\
\mathcal{A}_{\bar{a}\bar{\imath}\bar{e}\bar{n}} &= \langle \bar{a}\bar{e}\|\bar{\imath}\bar{n}\rangle + \langle \bar{a}\bar{n}\|\bar{\imath}\bar{e}\rangle + \delta_{\bar{\imath}\bar{n}}{}^{\beta} f_{\bar{a}\bar{e}} - \delta_{\bar{e}\bar{a}}{}^{\beta} f_{\bar{n}\bar{\imath}} \\
\mathcal{A}_{ai\bar{e}\bar{a}} &= \langle a\bar{e}\|i\bar{n}\rangle + \langle a\bar{n}\|i\bar{e}\rangle + \delta_{\bar{e}i}{}^{\beta} f_{\bar{n}\bar{a}} \\
\mathcal{A}_{\bar{a}\bar{\imath}fm} &= \langle \bar{a}f\|\bar{\imath}m\rangle + \langle \bar{a}m\|\bar{\imath}f\rangle + \delta_{m\bar{a}}{}^{\beta} f_{f\bar{\imath}}
\end{aligned} \tag{B.129}$$

Since the spin of the Fock matrices is accounted for by being either α or β Fock matrices, the spin on the label is superfluous. We can therefore write the $\mathcal{A}$ matrices in an understandable form as follows (and now using only one set of labels):

$$
\begin{aligned}
\mathcal{A}^{\alpha\alpha\alpha\alpha}_{aiem} &= \langle ae\|im\rangle + \langle am\|ie\rangle + \delta_{im}{}^{\alpha} f_{ae} - \delta_{ae}{}^{\alpha} f_{mi} \\
\mathcal{A}^{\beta\beta\beta\beta}_{aiem} &= \langle ae\|im\rangle + \langle am\|ie\rangle + \delta_{im}{}^{\beta} f_{ae} - \delta_{ae}{}^{\beta} f_{mi} \\
\mathcal{A}^{\alpha\alpha\beta\beta}_{aiem} &= \langle ae\|im\rangle + \langle am\|ie\rangle + \delta_{ei}{}^{\beta} f_{am} \\
\mathcal{A}^{\beta\beta\alpha\alpha}_{aiem} &= \langle ae\|im\rangle + \langle am\|ie\rangle + \delta_{ma}{}^{\beta} f_{ei}
\end{aligned}
\tag{B.130}
$$

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BIOGRAPHICAL SKETCH

Walter John Lauderdale was born on October 5, 1962, in the city of Pasadena, California, the home of the Rose Parade. In 1969, he and his family moved to Arcadia, California, where he finished most of his pre-college education. Mr. Lauderdale graduated as salutatorian from Arcadia High School in June, 1980 and having received an appointment to the United States Air Force Academy, reported to that institution later in June. After an informative introduction to military life, he declared Chemistry as his academic major one month into the 1980-1981 school year. After completing a well-rounded academic and military education, he graduated from the Academy with an ACS accredited Bachelor of Science degree in Chemistry in May, 1984. Upon receiving his comission as a second lieutenant in the Air Force, he reported to duty at the Air Force Rocket Propulsion Laboratory, Edwards AFB, in July, 1984, where he began doing basic chemical research into rocket propellant oxidizers.

After conducting some syntheses of several powerful explosives, he decided that perhaps theory was a better way to achieve fame and fortune. While also modelling molecular systems using a variety of theoretical tools, doing some non-synthetic experimental work, managing some basic research contracts with universities and industry, he slipped in some graduate work leading to the award of a Master of Science degree in Chemistry from California State University at Northridge in January 1989. During this period, he was selected by the Air Force to continue his studies towards a Ph.D. degree, specializing in theoretical chemistry techniques. It was at this point that now Captain Lauderdale came to the University of Florida. After three years at UF, he has completed his requirements for the Ph.D. and will be stationed at his alma mater, the USAF Academy, in January 1992.

Captain Lauderdale has had the pleasure of becoming a married man while at UF, his wife being the former Miss Susan Henry of Gainesville. After three years of school in Florida, he is looking forward to another change of scenery.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Rodney J. Bartlett, Chairman
Graduate Research Professor of Chemistry
and Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Willis B. Person
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William Weltner
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

N. Yngve Öhrn
Professor of Chemistry and Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Professor of Physics

This dissertation was submitted to the Graduate Faculty of the Department of Chemistryin the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1991

Dean, Graduate School